Electrolysis research at SINTEF / NTNU

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Workshop on Materials Process Engineering

San Francisco February 19.

Outline

- SINTEF
  - What is SINTEF?
  - Organisation
- Electrolysis Research Topics
  - Aluminium – main part
  - Silicon
  - Titanium (ref. K. Dring)
  - Iron (ref. Prof. Haarberg)
  - Ionic liquids

SINTEF

Technology for a better society

SINTEF

The Foundation for Scientific and Industrial Research at the Norwegian Institute of Technology

The Norwegian University of Science and Technology (NTNU)

Campus

A Technological Cluster with Education, Basic and Applied Research

Located in Trondheim (1500) and Oslo (500).

One of the largest independent research institutes in Europe.

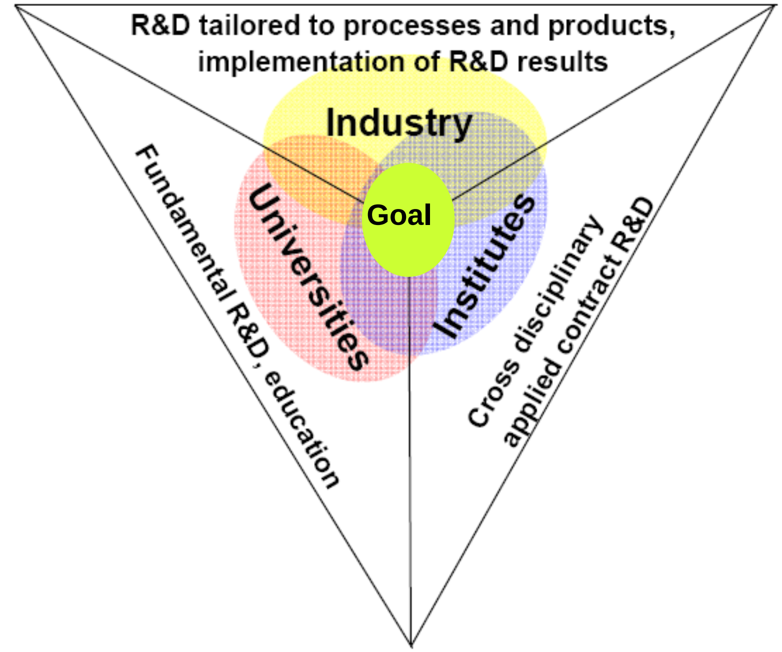
OUR

Partners

- The Norwegian University of Science and Technology, NTNU
  - 20000 full-time students
  - 1000 scientific personnel
- University of Oslo, UiO,
  Faculty of mathematics and natural sciences
  - 4500 full-time students
  - 520 scientific personnel

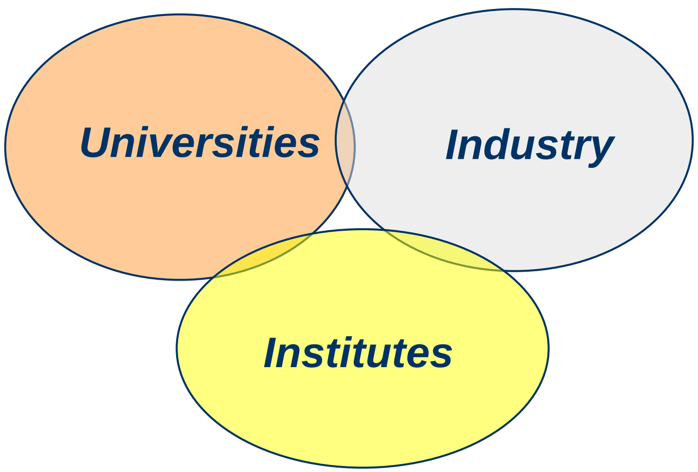
NTNU and the SINTEF Group Collaboration in R & D

The Norwegian Collaborative R&D



Partnership with three different players:

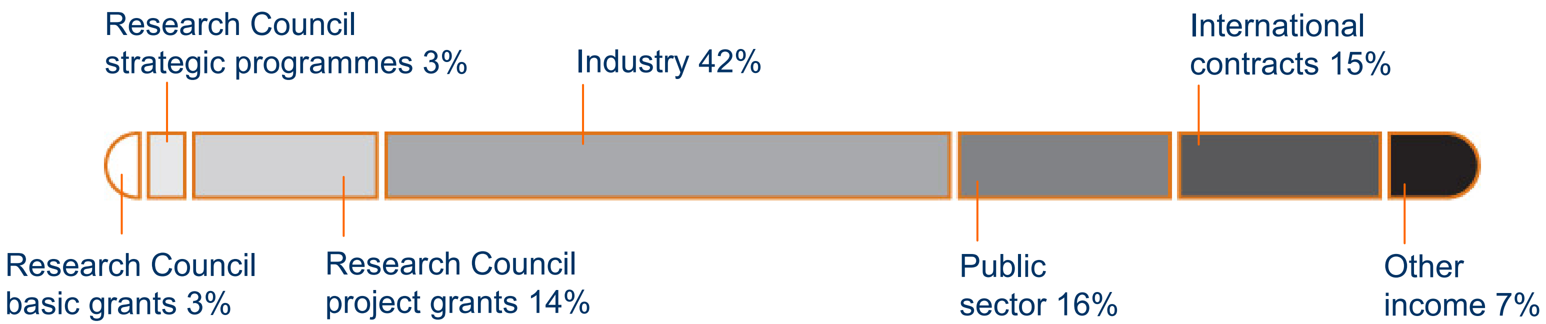
- Having slightly different roles
- Working towards the same common goal



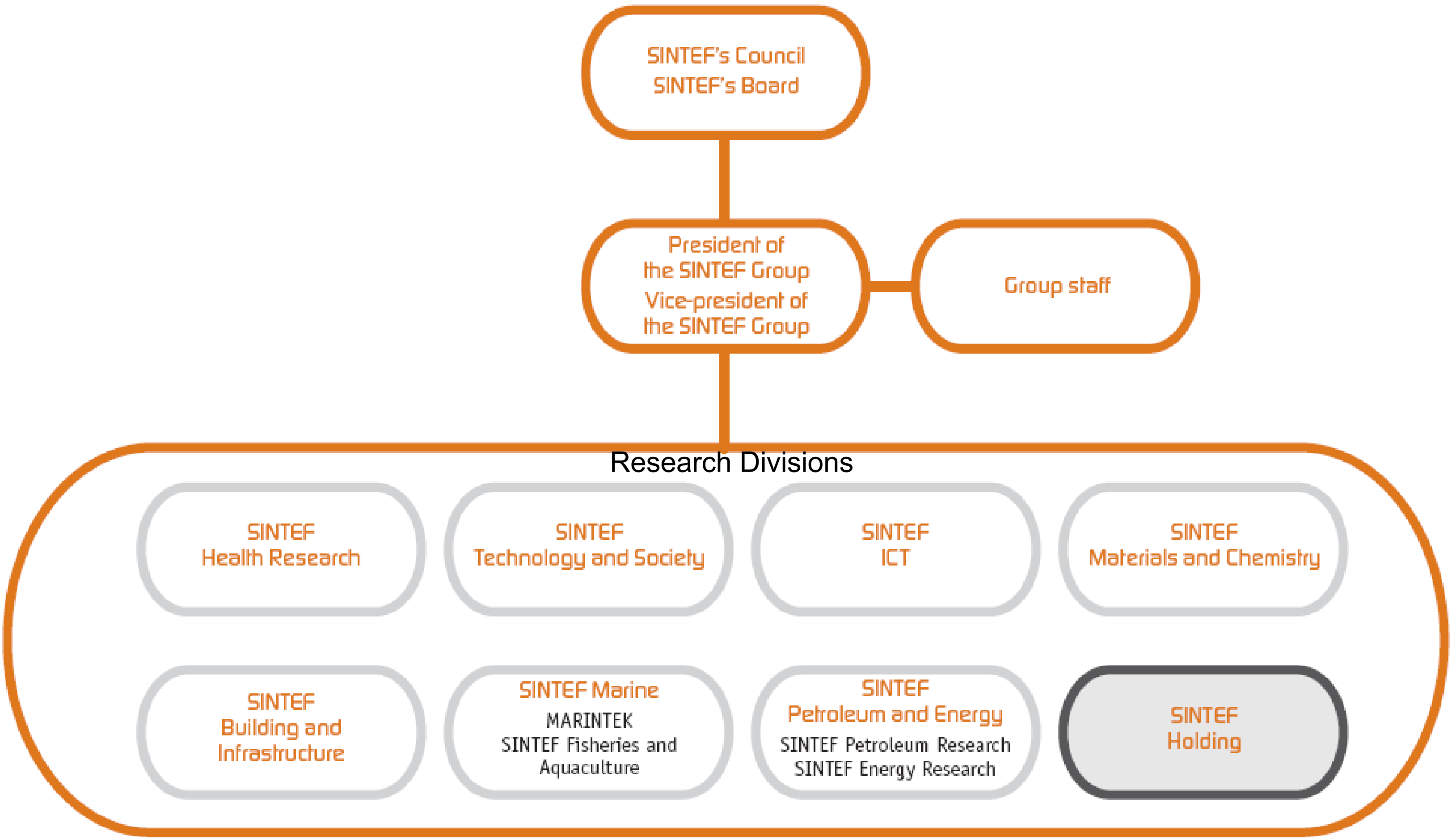
The collaboration model contributes to:

- Industrial focus at the R&D institutions
- Scientific quality in the research

The SINTEF Group sources of finance



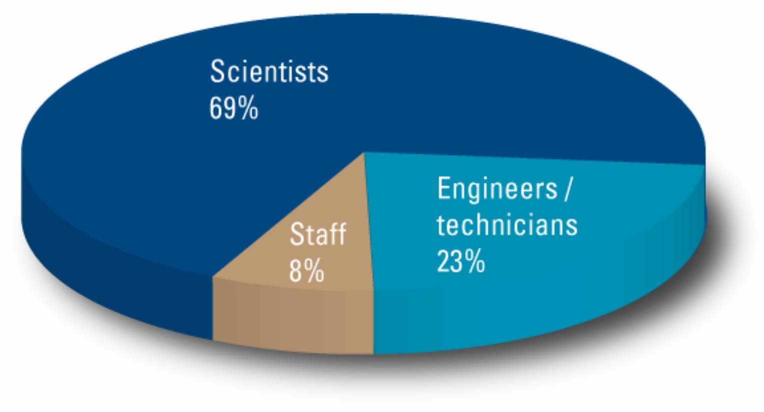
SINTEF Group. Organization chart.

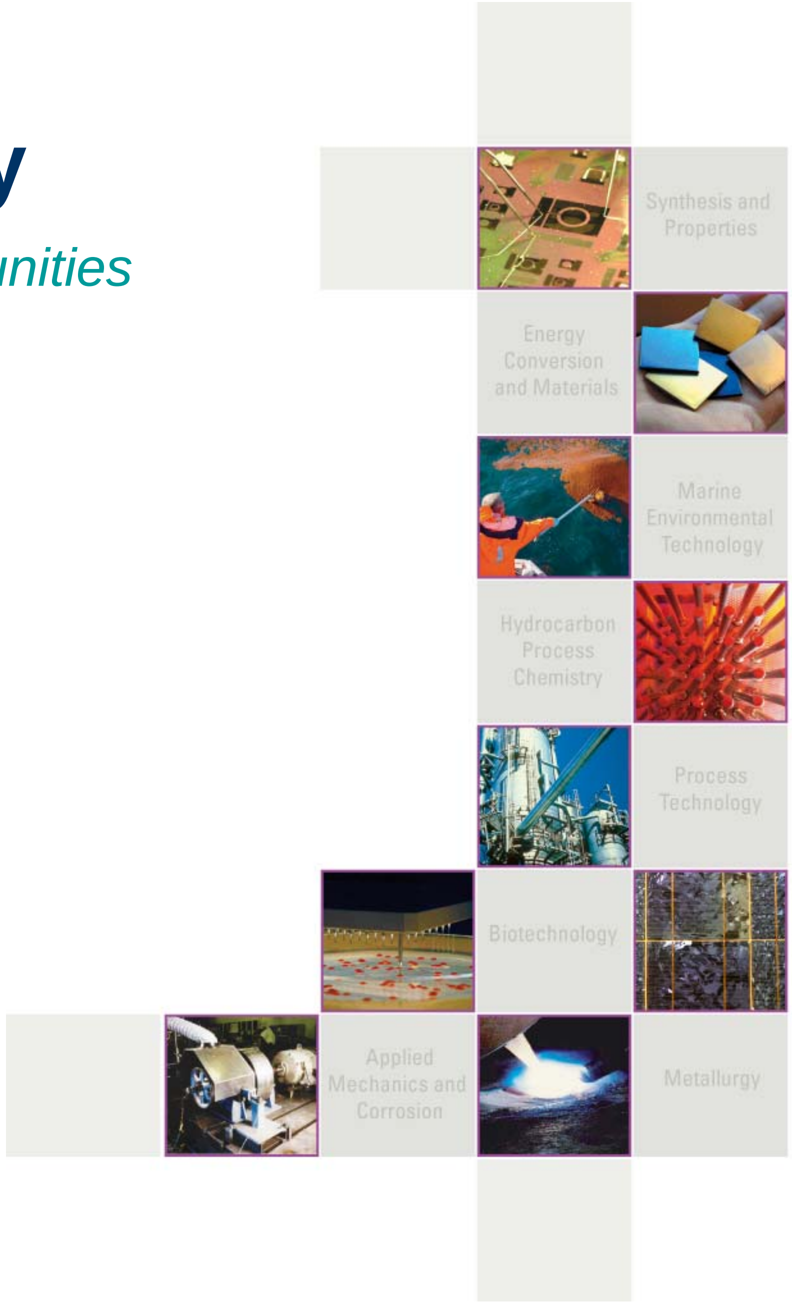


Materials and Chemistry

From ideas to business opportunities

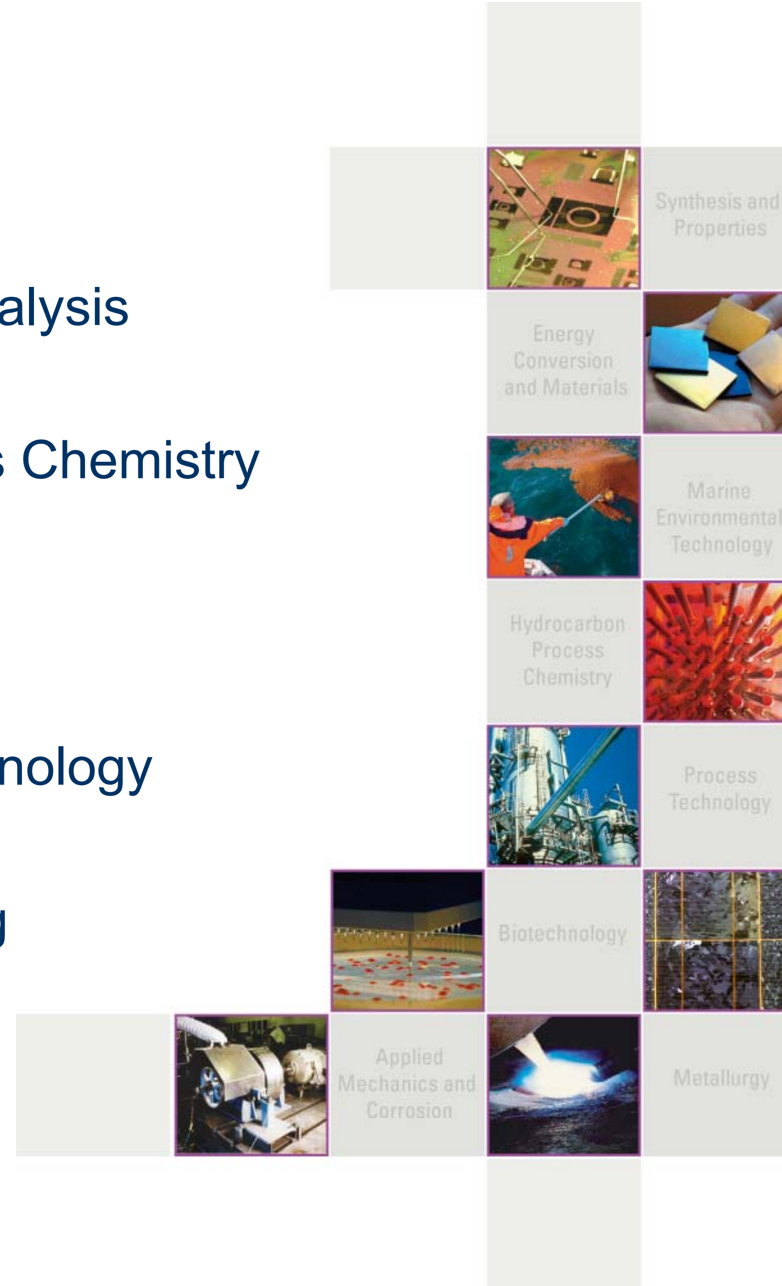
400 employees



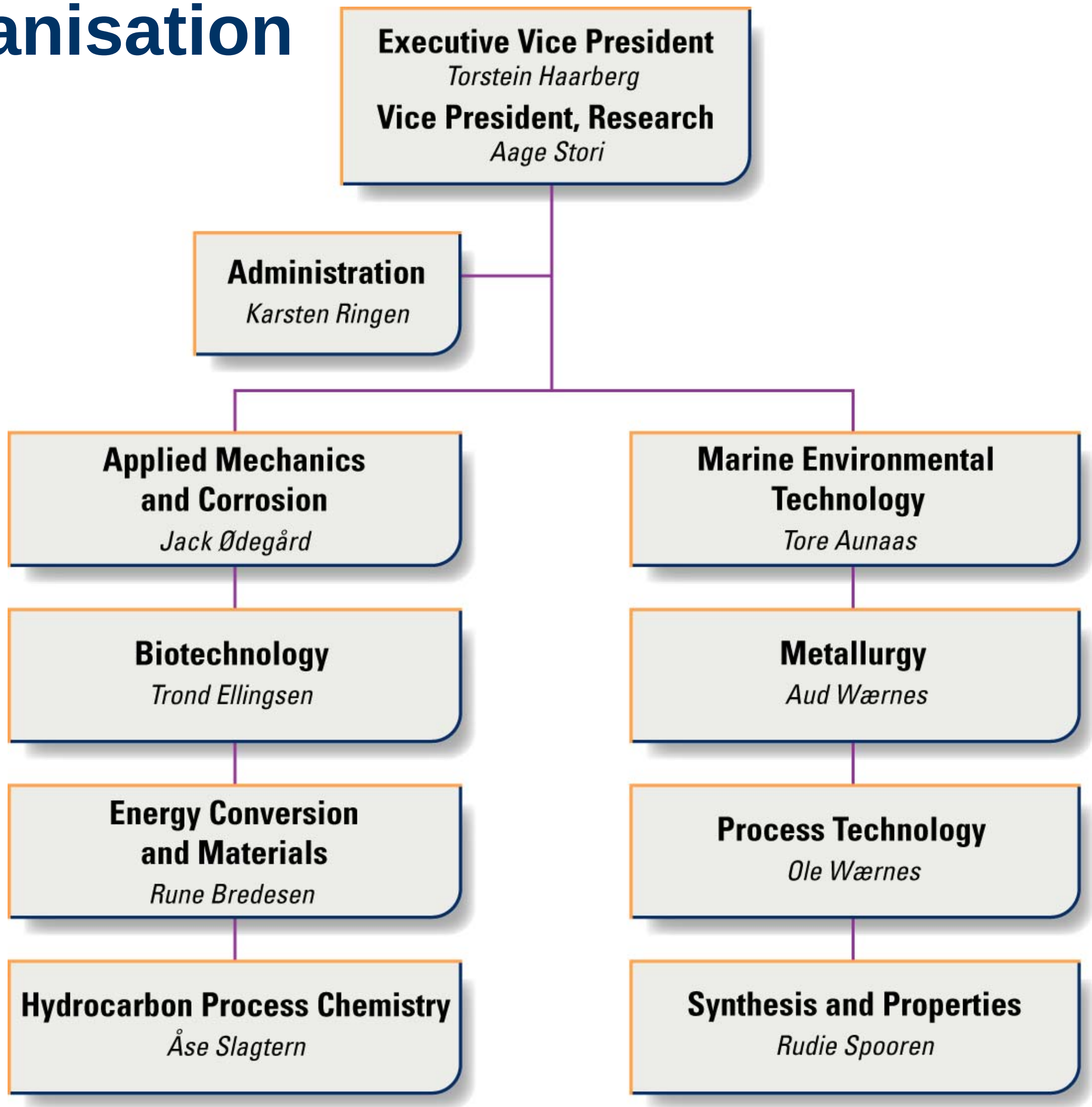


Areas of research

- Advanced Characterization and Analysis
- Biotechnology
- Chemical Engineering and Process Chemistry
- Energy Conversion
- Environmental Technology
- Flow Technology
- Functional Materials and Nanotechnology
- Materials Performance
- Materials Production and Recycling
- Modeling and Simulation
- Processing and Manufacturing
- Synthesis and Testing



Organisation



2004-12-15

Energy Conversion and Materials Research Teams

Research Director Rune Bredesen

- Electrolysis (6)
  Research Manager Egil Skybakmoen
- Inorganic Materials Chemistry (11)
  Research Manager Arne Petter Ratvik
- Energy Conversion (5)
  Research Manager Ann-Mari Svensson
- Functional Ceramics (6)
  Research Manager Christian Simon
- Materials for Energy and Environmental Technology (9)
  Research Manager Partow Henriksen

Main fields
Energy Conversion and Materials

- **Electrolysis**
  - Aluminium electrolysis
  - New processes SoG-Si, Ti, Fe, carbon nano tubes
  - Ionic liquids
- **Inorganic Materials Chemistry**
  - Refractories and ceramics
  - Carbon materials science – electrodes
  - Powder- and nano technology
- **Energy Technology**
  - Fuel cells, solar energy, hydrogen energy, etc
- **Functional Ceramics**
  - Membranes, coatings, nano-technology, etc
- **Energy technology and environmental technology**
  - Gas membranes, CO_2- capture, etc

Ana Maria Martinez
Research Scientist

Egil Skybakmoen
Research Manager

Asbjørn Solheim
Senior Scientist

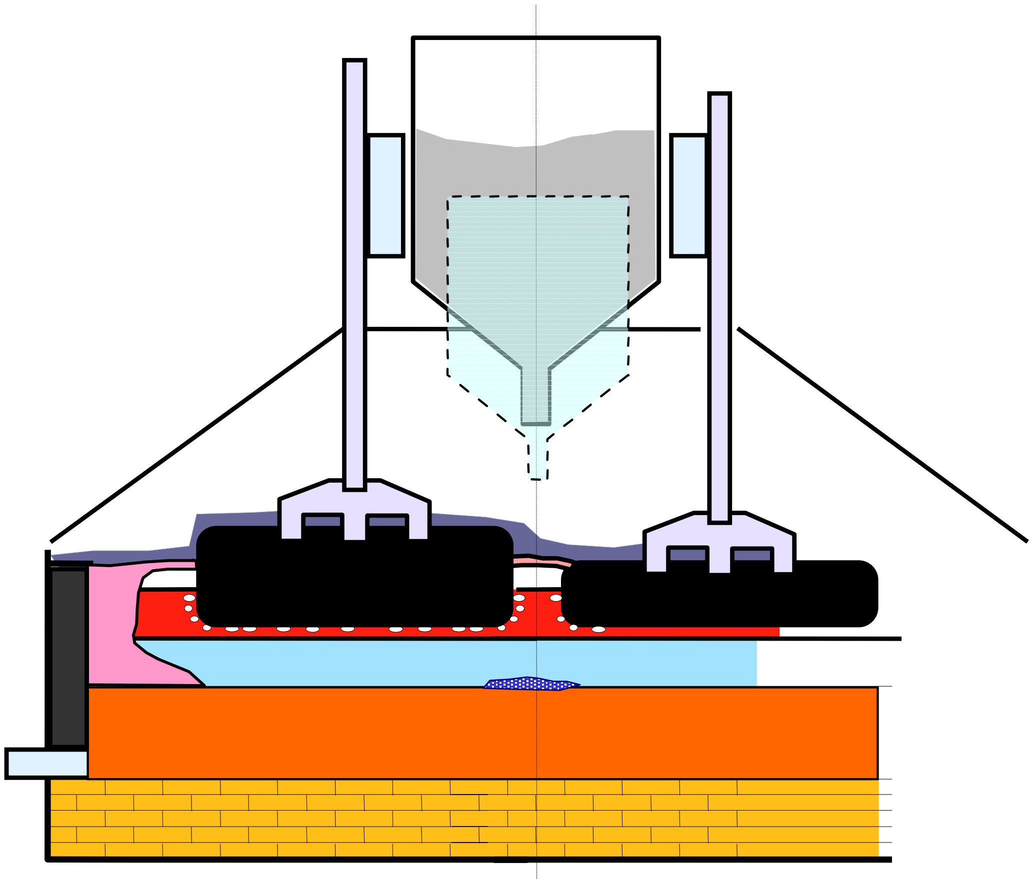
Electrolysis team 2009

Karen Sende Osen
Research Scientist

Sverre Rolseth
Senior Scientist

Henrik Gudbrandsen
Research Engineer

Aluminium



Energy: 13 – 15 kwh/ton Al
Use around 2000 kg alumina, 500 kg Carbon to produce1000 kg Al (and 1500-2000 kg CO_2)

Why Aluminium in Norway ?

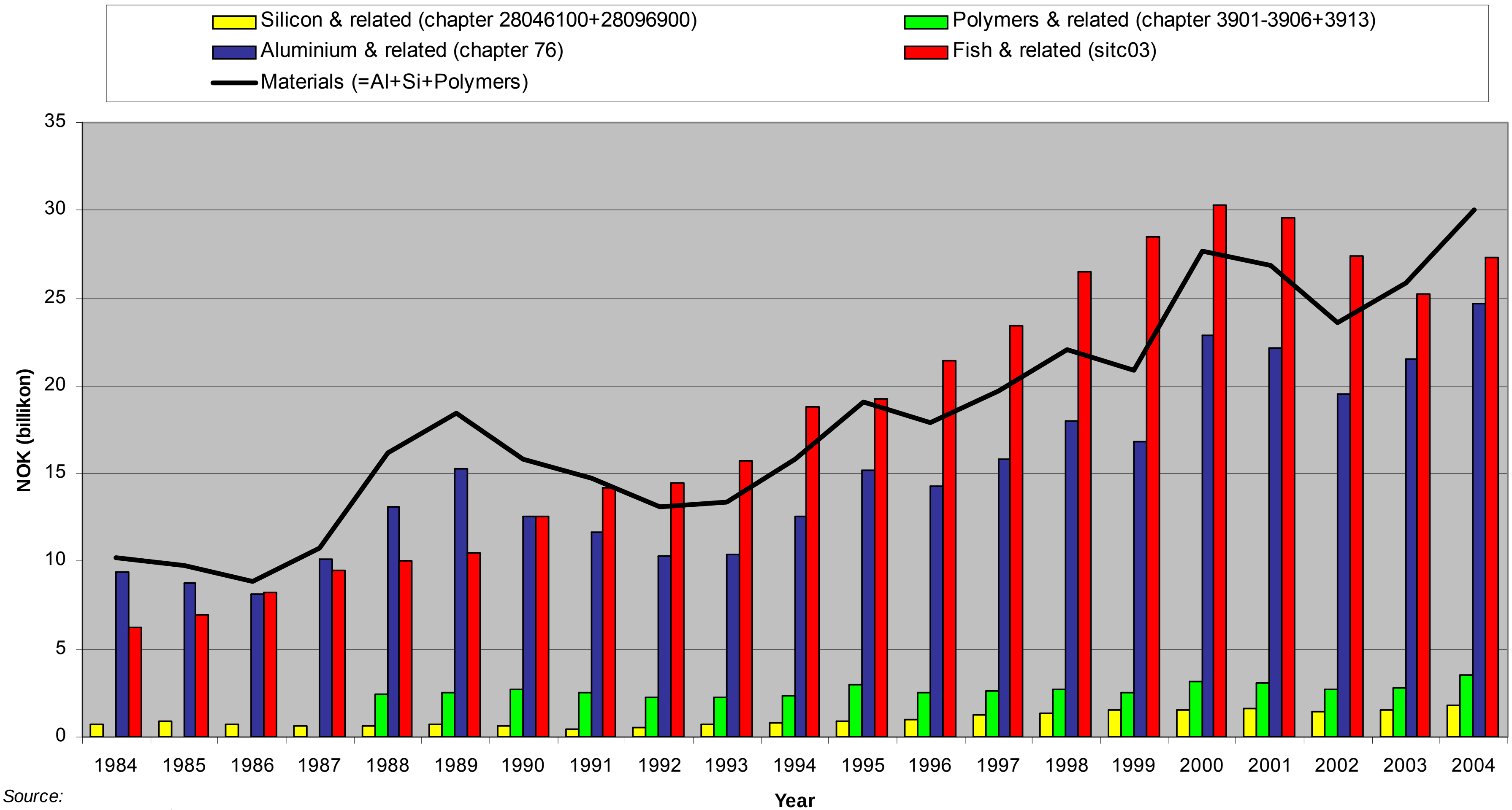
- Low-priced energy – water power – political reasons
  - But energy prices increasing now….long-term contracts going out.
- Hydro Aluminium
  - Has its own cell-technology (HAL 420+).
  - Karmøy - 295 000 t Al/y (125 000 t Søderberg, 170 000 t Pre-bake)
  - Sunndalsøra – 340 000 t Al/y (all pre-bake, new plant 2004)
  - Årdal- 226 000 t Al/y (50 000 t Søderberg, 176 000 t Pre-bake)
  - Høyanger – 76 000 t Al/y (23 000 t Søderberg, 53 000 t Pre-bake)
  - Bought VAW 2002 – plants in Germany, Canada, Australia.
  - New plant in Qatar planned around 2010 – 570 000 t Al/y
  - Søderberg out in 2007 (Høyanger, Årdal) and 2009 at Karmøy.
- Elkem Al (100 % Alcoa from 2009)
  - Mosjøen – 185 000 t Al/y (all pre-bake). New anode carbon plant finished 2007.
  - Lista - 100 000 t Al/y (all Søderberg)
- Sør-Norge Al (51 % Alcan, 49 % Hydro Al)
  - Husnes – 170 000 t Al/y (all Pre-bake)

Søderberg plant

Modern Pre-bake line - Sunndalsøra

SINTEF Materials and chemistry
21-01-2005 2005 Egil Trømborg

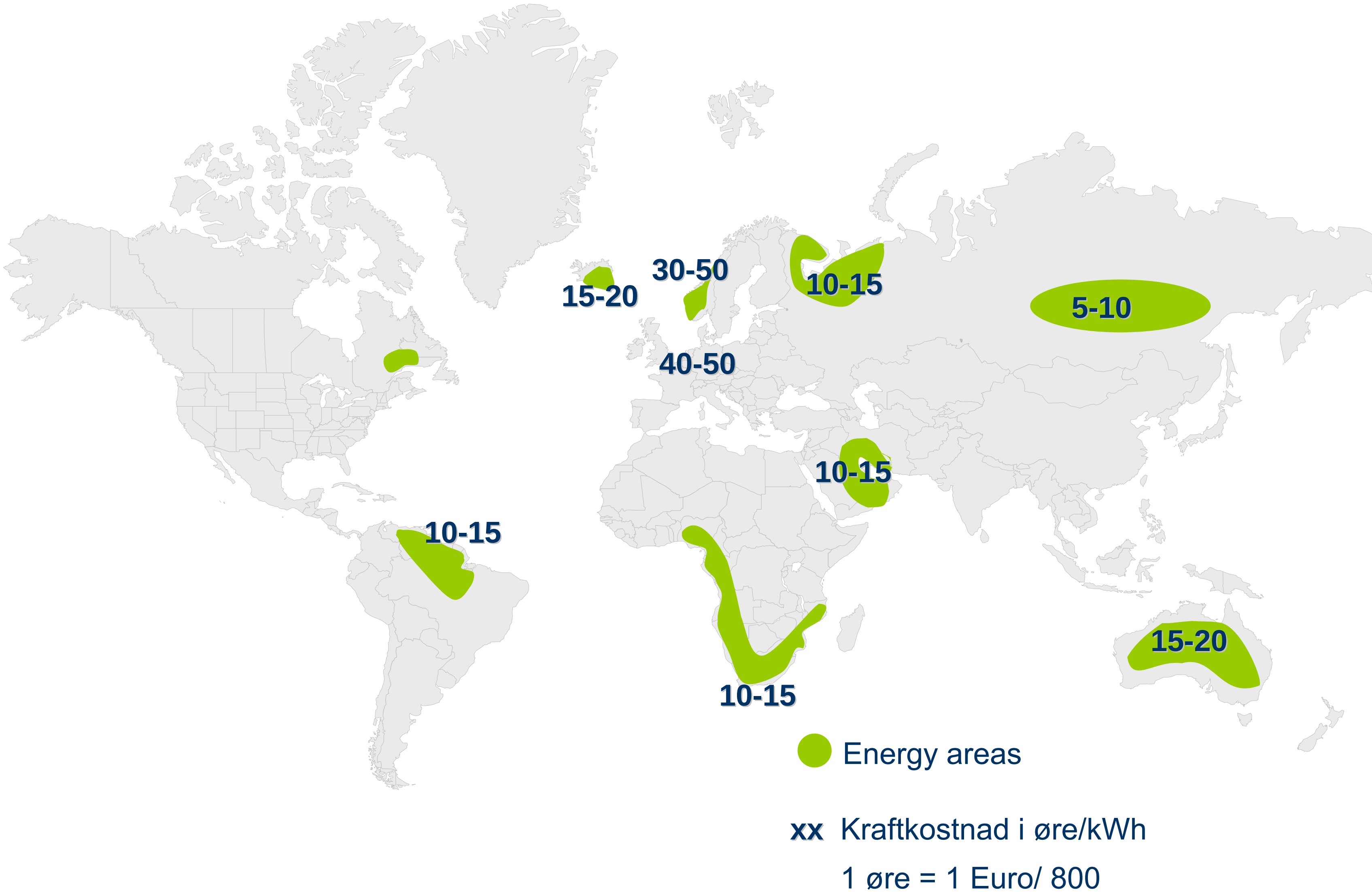
EXPORT VALUES FROM NORWEGIAN INDUSTRY



Source:
IStatistisk sentralbyrå (Nina Rolsdorph, Konsulent, Seksjon for utenrikshandel)

Energy cost world-wide

From Hydro Aluminium, january 2007



Aluminium Electrolysis

More than 30 years research cooperation with the Norwegian Aluminium industry has led to significant process improvements. Some projects/fields:

Current Efficiency

Bath Chemistry

Properties of Alumina

Electrode Mechanisms

Cell Life

Failure Mechanisms

Refractory Technology

Recirculation of Materials

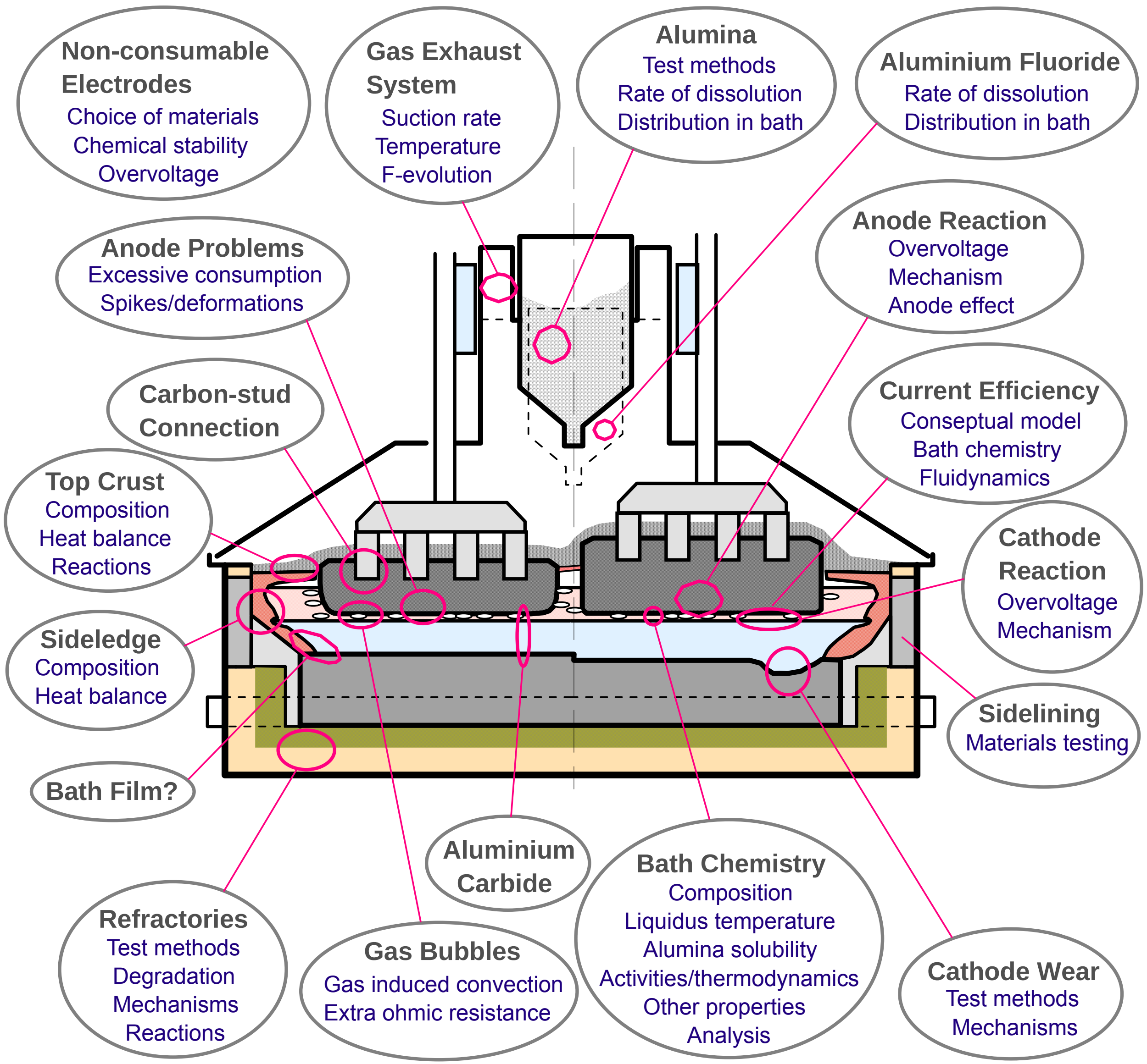
Non-oxide Ceramics

New Processes

Fluid Flow Modelling

Inner and Outer Environment

Primary Aluminium Research at SINTEF



- The primary aluminium group at SINTEF/NTNU has in average 10 scientific publications per year
- Actively involved in the work of many of the PhD candidates educated at NTNU

Field of Research

- Traditionally only primary production of Al – a long and strong co-operation with the Norwegian Al industry and NTNU. Recruitment. Ph-D students.

- High temperature lab. – molten salts from 600 – 1600 °C.
  - Electrochemical measuring methods (cyclic voltametry etc…). Electrode reactions.
  - Systematic mapping of electrolyte properties – fluoride melts, mainly.
  - Analytical methods (LECO for oxide content in melts). Na-content in metal.
  - Current efficiency (optimal cathode reaction).
  - Measurements on industrial cells (CE, distance electrodes, anodic overvoltage, flow pattern electrolyte, metal, liquidus temperatures etc.
  - Test methods – graphite cathode – anode – refractories.
  - Modeling – heat balance, flow pattern (FLUENT)
  - Voltage balance – save energy.
  - Anode slots – gas evolution. Modeling.
  - Development of sensors (oxide content in situ, AlF_3-content in situ)
  - Gas driven flows – gas bubble resistance.
  - HF- formation – climate gases (CF_4, C_2F_6)

Projects: Al-related topics

- CarboMat (Ended 2006)
  - RCN, Hydro Al, Elkem, Søral, Statoil and Ferro-alloy industry
- ThermoTech (Degradation linings, modeling) Ended 2008
  - RCN, Hydro Al, Elkem, Søral, Statoil and Ferro-alloy industry
- DuraMat (starts 2009).
  - Hydro Al, Alcoa Norway and Søral and RCN
- Hydro Al
  - Some projects related to the days process (confidential)
  - Also projects partly financed by RCN (5 year program started 2006)
- Others
  - For instance SGL-Carbon (graphite cathode materials)
- Testing Refractories
  - Suppliers world-wide (SiC-based sidelinings and bottom linings)
  - Alilab (Al-industries refractories lab. at SINTEF)

Primary Al Research
Future challenges

- Energy recovery
  - Low temp. concepts
  - High temp. concepts
- CO_2-capture
  - Is it possible? – economic?
- Raw materials
  - Anode quality
  - Alumina
- Metal quality
  - Impurities
- Energy efficiency (voltage drop in cell components)
- Process control systems
  - sensors for cont. temp./ AlF_3 / Al_2O_3

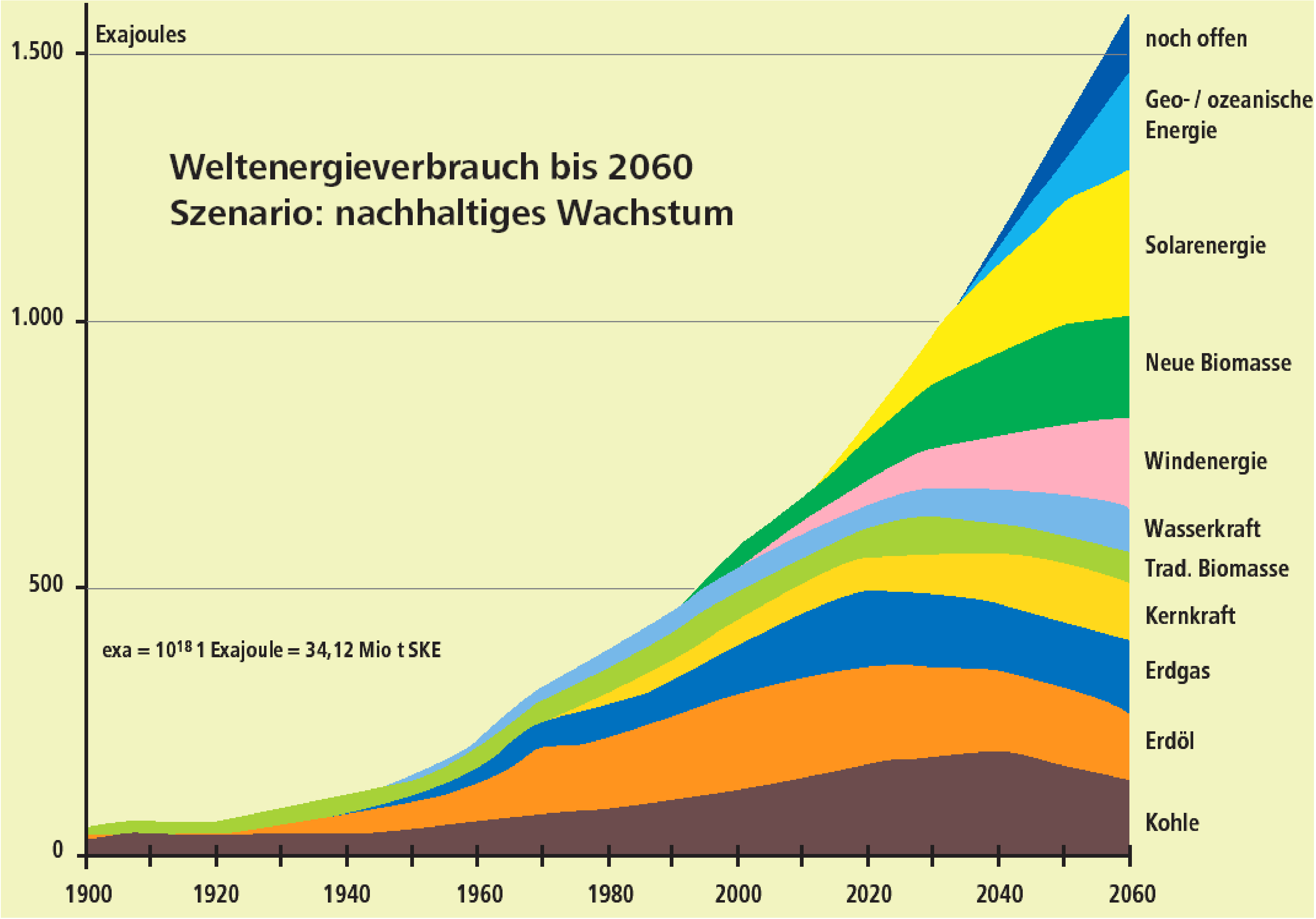
Primary Al Research
Future challenges

- Increased lifetime of cell
  - Cathode wear – the main problem today!
  - Linings
  - New improved materials

- Reduced SPL
  - Reuse linings?
- Fluoride emmisions
  - HF
  - CF_4 / C_2F_6 (no anode effects)
- Alternative processes for Al electrowinning
  - Inert electrodes – still a topic for Alcoa and Rusal…
  - Alternative electrolytes
  - Gas-electrodes (Gassmaks project)
  - Carbothermic process (Alcoa-Elkem)

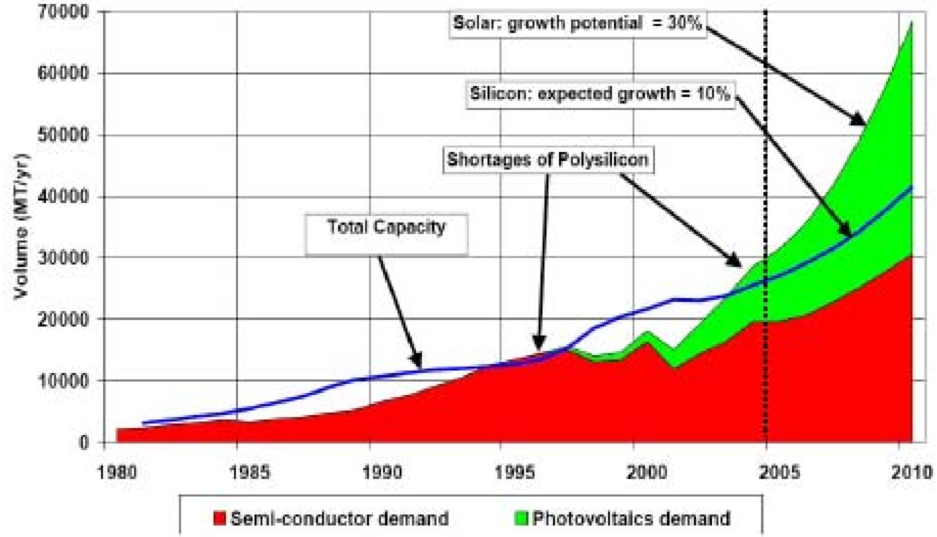
Solar Grade Silicon

The worlds need energy – clean energy



New technologies for production of SoG Si

- Today, there is a lack of solar grade silicon due to increased production and use of solar cells
- New processes to produce SoG Si must be developed



- Technologies being industrialized:
  - Carbothermic reduction with purification
  - Direct carbothermic reduction from pure raw materials
  - Reduction with zinc
- Electrochemical methods under development:
  - Electrochemical refining of MG-Si
  - Electrochemical deposition of Si
  - Deoxidation of solid SiO_2

Source: Wacker 2nd SoG Si Workshop

Electrochemical Silicon at SINTEF and NTNU

❶ Si electrolysis from $CaCl_2$-CaO-SiO_2 at 850°C

E.Olsen, ” Electrolyte and method for manufacturing and/or refining of silicon”, PCT WO 2002/099166 A1

❷ EU project FoXy, WP3: Electrochemical refinement of metallurgical feedstock at 700-850°C

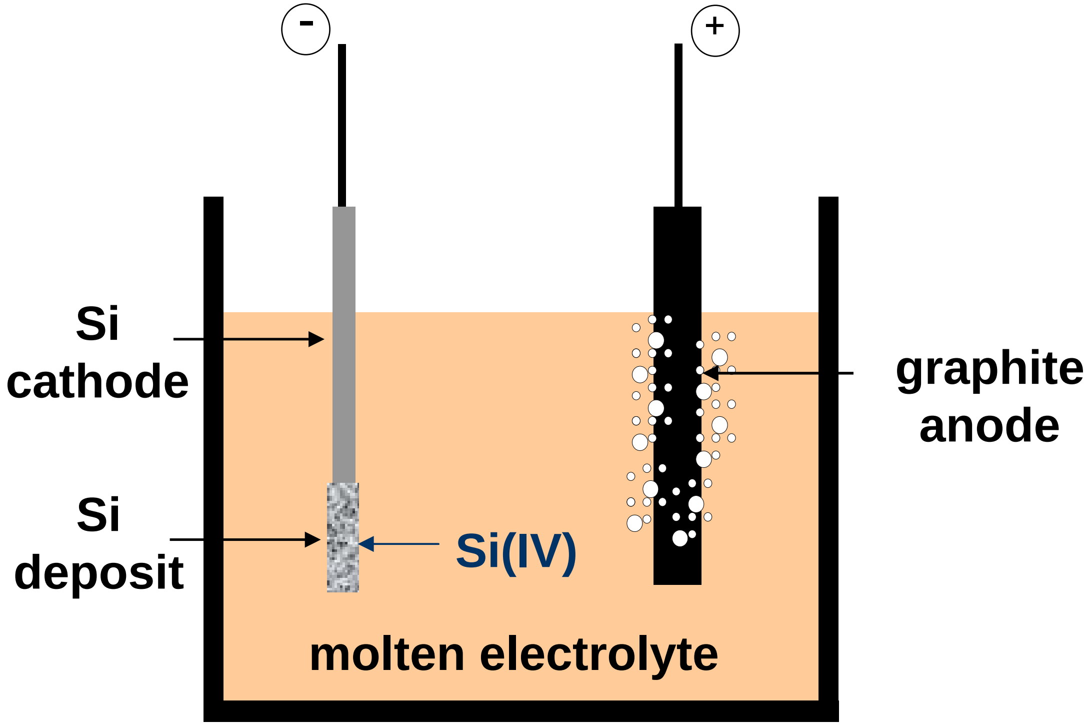
❸ Refining of **liquid** Si in fluoride melts-”3 layers process” at above 1450°C

E.Olsen, ”Electrolyte and method for electrochemical refining of Silicon”, PCT WO 2008/115072 A2

Si electrolysis

Electrolyte: $CaCl_2$- CaO (10wt%) - SiO_2

T= 850^{o}C

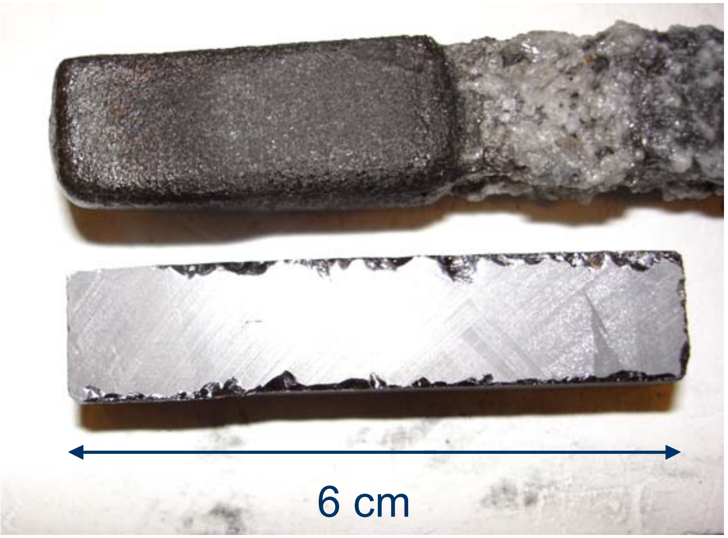


☞ cathode reaction:

$Si(IV) + 4e^{-} \rightarrow Si\ (s)$

☞ anode reaction:

$C(s) + 2\ O^{2-} \rightarrow CO_2\ (g) + 4e^{-}$



Electrochemical refining of Si

Principle

☞ anode reaction:

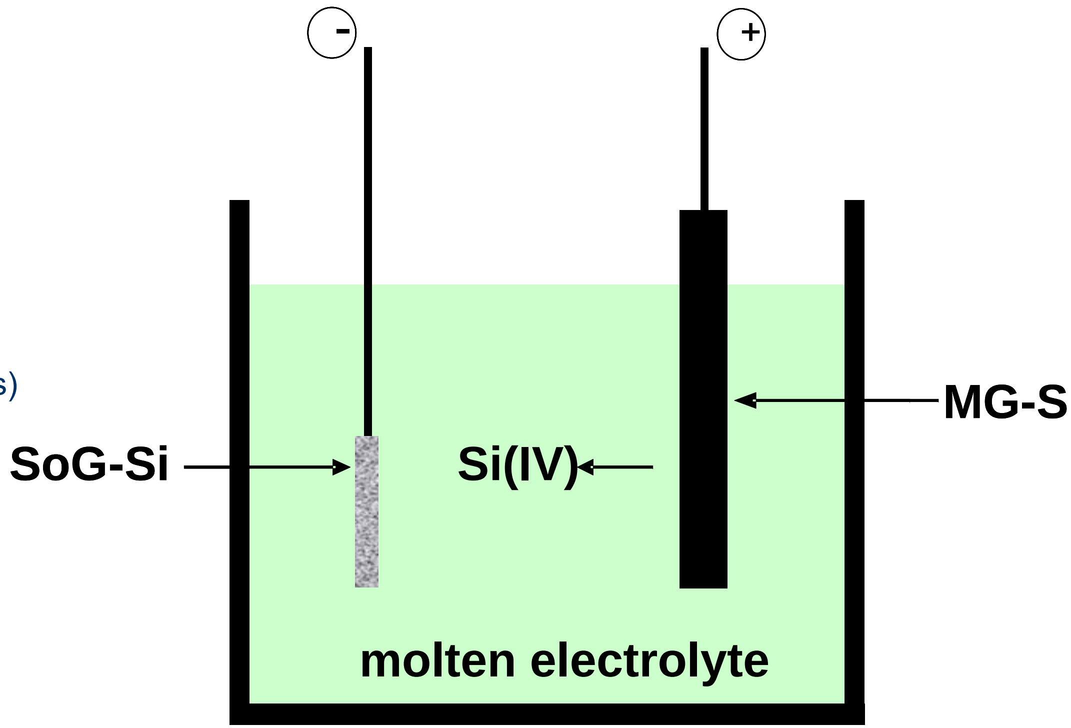
$Si_{(with\ impurities)} \rightarrow Si\ (IV) + 4e^-$

☞ cathode reaction:

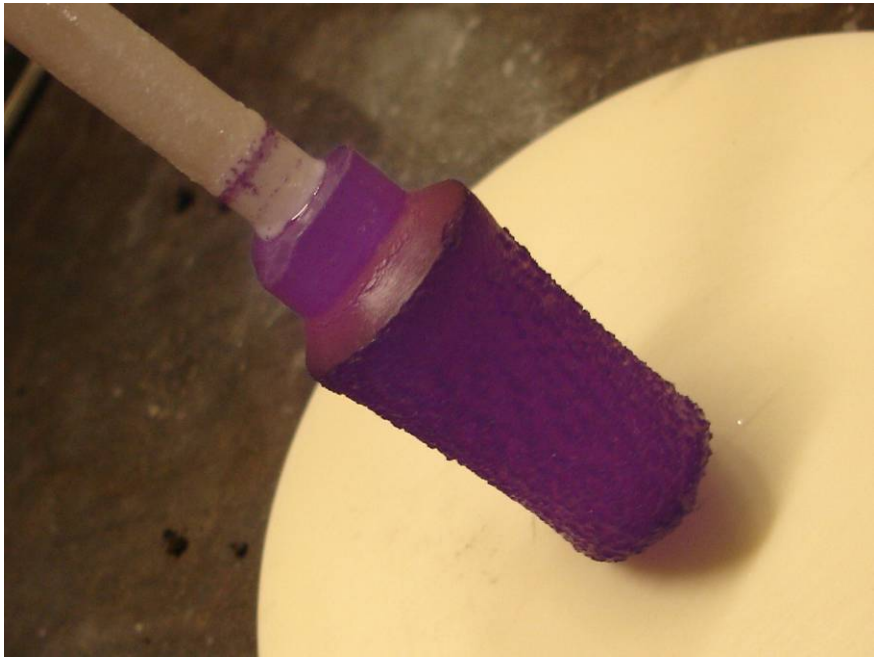
$Si\ (IV) + 4e^- \rightarrow Si_{(without\ impurities)}$

Elements less nobel than Si will not deposit at the cathode

Elements more nobel than Si will not dissolve anodically



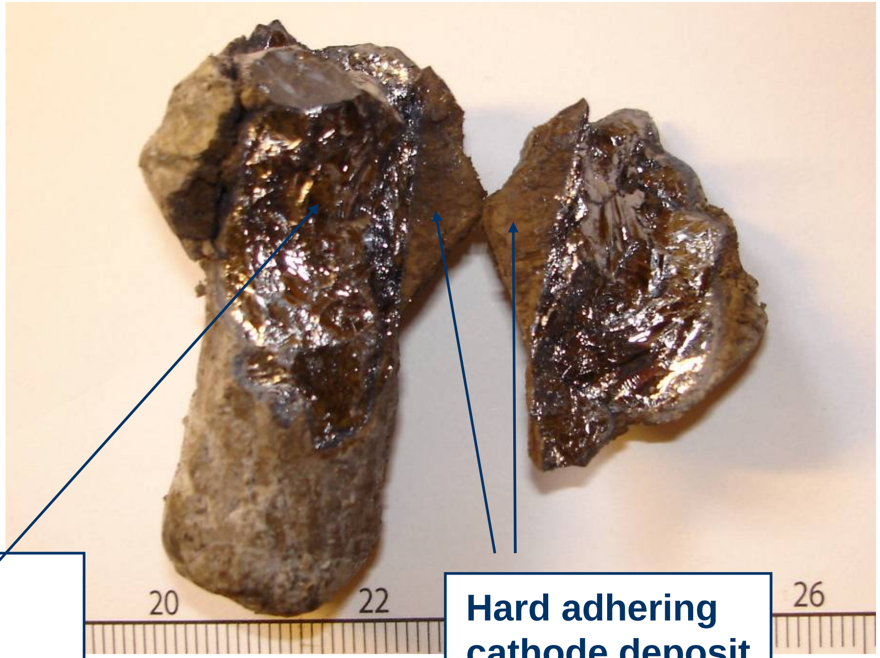
Removal (scraping off) cathode deposit



Used electrodes

Used anode, partly dissolved

Split cathode, with very hard deposit adhering (difficult to scrape off)



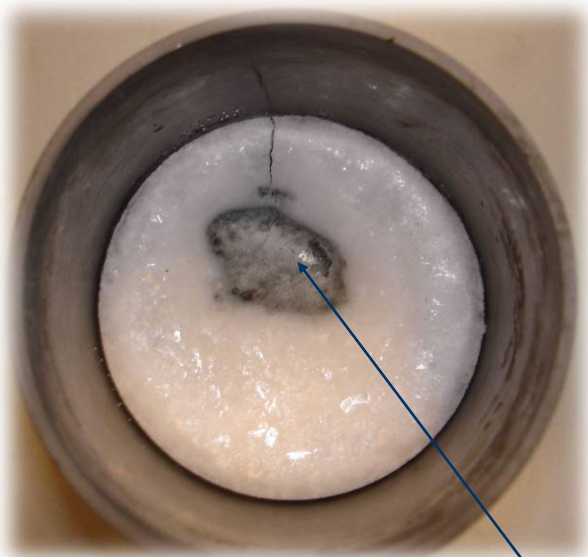
Original solar grade silicon material

Hard adhering cathode deposit

Treatment of cathode deposit

Scraped off deposit re-melted with a flux of CaF_2 under inert atmosphere in an induction furnace

Prior to re-melting: Deposit in glassy carbon crucible placed in induction furnace

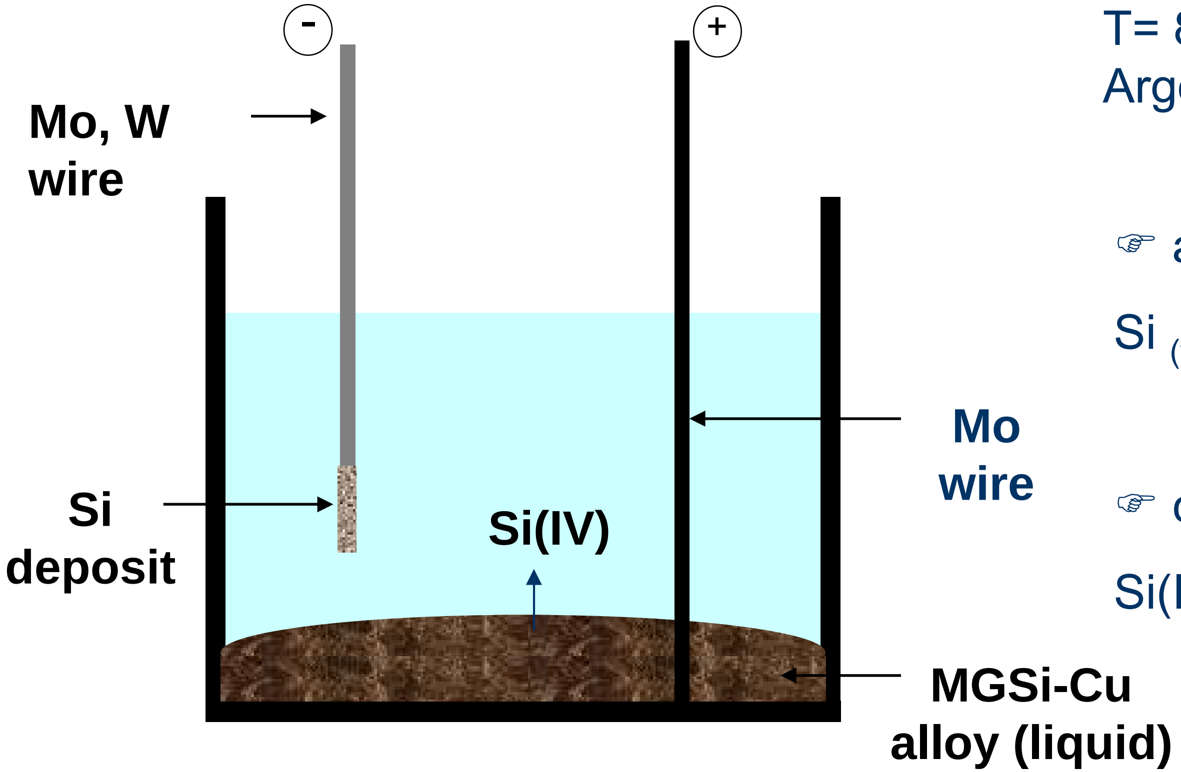


After melting of deposit: Si had coalesced into larger globules of coherent “metal”.

Broken globule of silicon that could easily be separated from the frozen flux.

Electrochemical refining of Si

- Refining of Si in chloride melts



Electrolyte composition:
$CaCl_2$–CaO–NaCl–Si (80:10:5:5 mol%)

T= 850 °C
Argon atmosphere

- anode reaction:

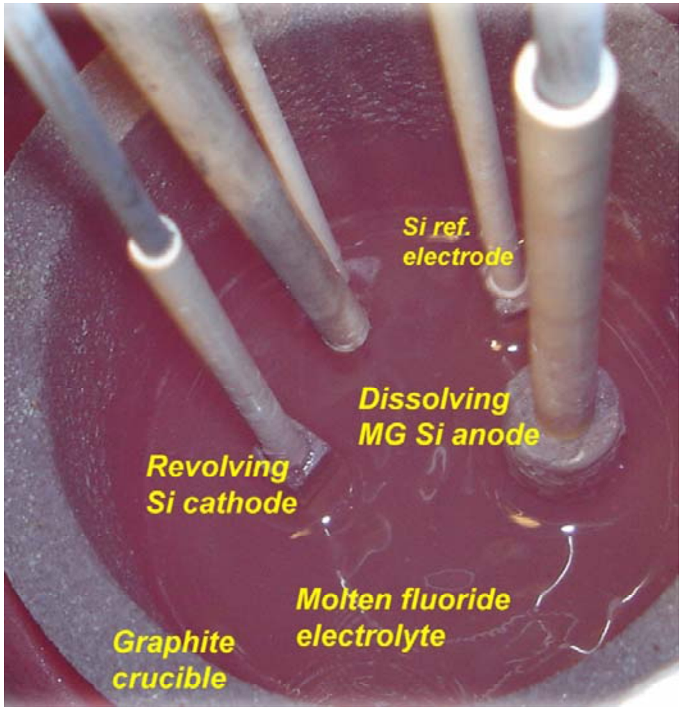
Si (with impurities) → Si(IV) + $4e^-$

- cathode reaction:

Si(IV) + $4e^-$ → Si (without impurities)

Electrochemical refining of Si

- Refining of Si in fluoride melts



Electrolysis cell

Removing deposit

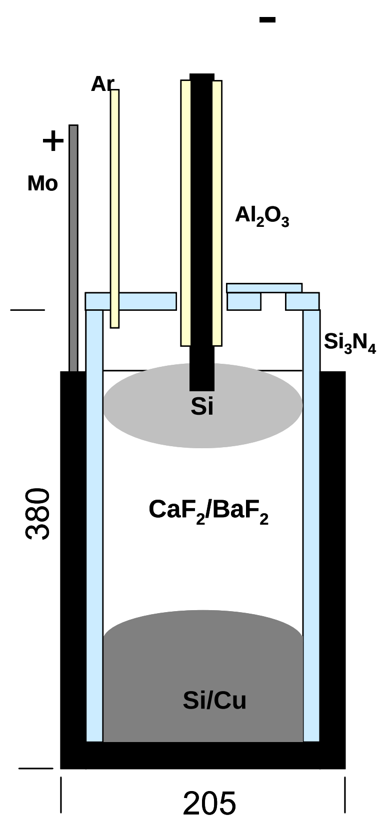
Used anode

Silicon

1 U. Cohen, “Some prospespective application of silicon deposition from molten fluorides to solar cell fabrication”, Journal of Electronic Materials, Vol. 6, No.6, (1997).
2 G. Rao, D. Elwell, and R.S. Feigelson, ”Electrowinning of Silicon from K2SiF6-Molten Fluoride System”, J. Electrochem. Soc., Vol. 127, No. 9, pp. 1940-1944 (1980).
3 J. De Lepinay J. Bouteillon et.al, “Electroplating of silicon and titanium in molten fluoride media”, J. Appl. Eelectrochem., Vol. 17, pp. 294-302 (1987).

High temperature electrochemical refining of Si

- Refining of liquid Si in fluoride melts-”3 layers process”



weight/g	height/cm	density g/cm^3
2000	4	2.57
6800	12	2.8
4000	6	3.5

- E.Olsen, ”Electrolyte and method for electrochemical refining of Silicon”, PCT WO 2008/115072 A2

Titanium


Titanium
Atomic symbol :Ti
Atomic Number: 22
Atomic Radius: 144.8 pm
Melting Point: 1668 C
Atomic Weight: 47.90
Boiling Point: 3287 C
Electron Configuration: [Ar]4s23d2
Oxidation States: 4,3,2
9 6 2007

Titanium electrolysis

Since autumn 2006, SINTEF together with NTNU participate in a project supported by the Norwegian Research Council and Norsk Titanium AS

① Electrodeoxidation of TiO_2 cathodes in molten chlorides

② Electrowinning of Ti from TiO_xC_y anodes

Electrodeoxidation of TiO_2

FFC Cambridge Process

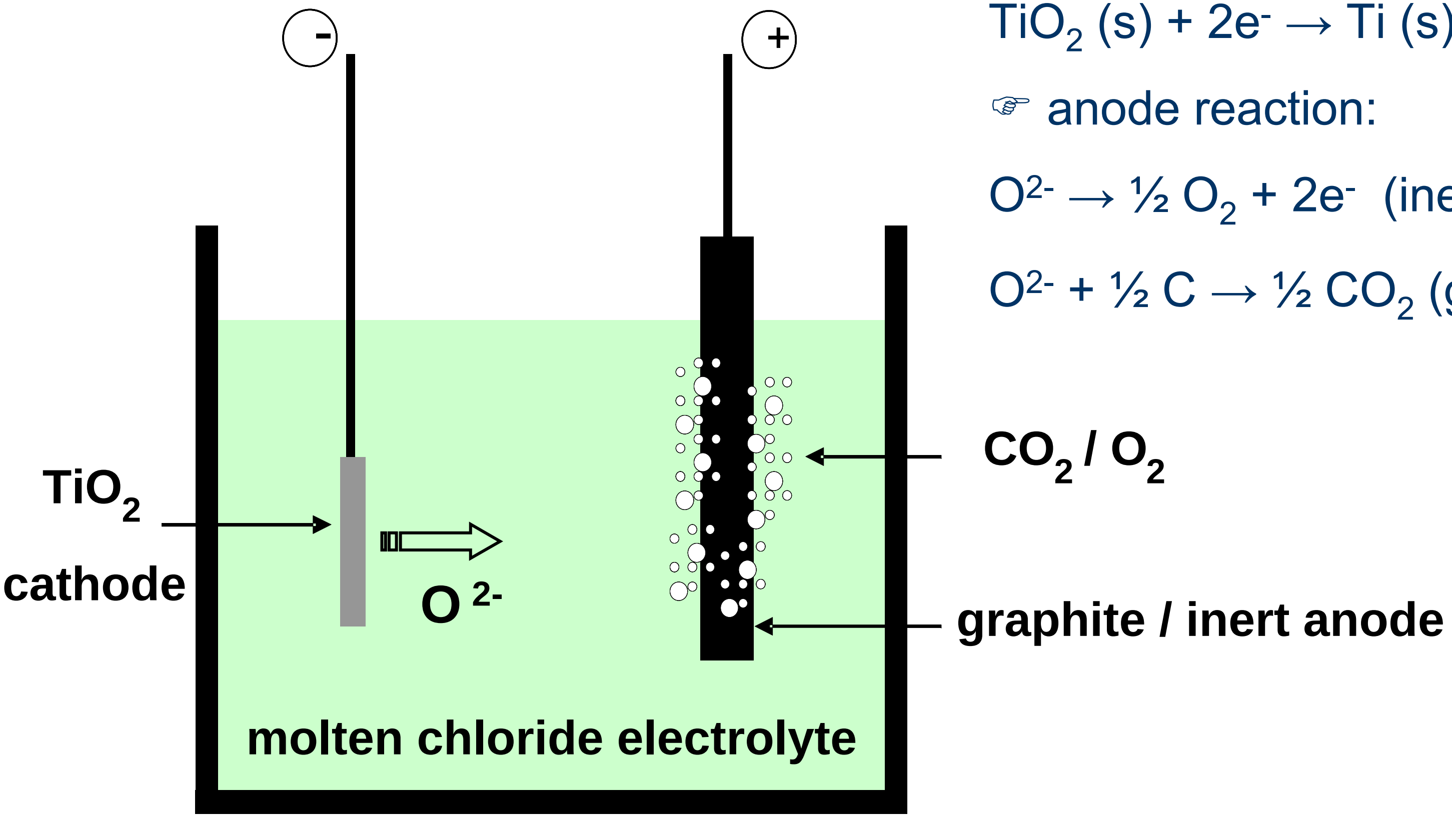
- cathode reaction:

TiO_2 (s) + 2e$^-$ → Ti (s) + O^{2-}

- anode reaction:

O^{2-} → ½ O_2 + 2e$^-$ (inert anode)

O^{2-} + ½ C → ½ CO_2 (g)+ 2e$^-$ (C anode)



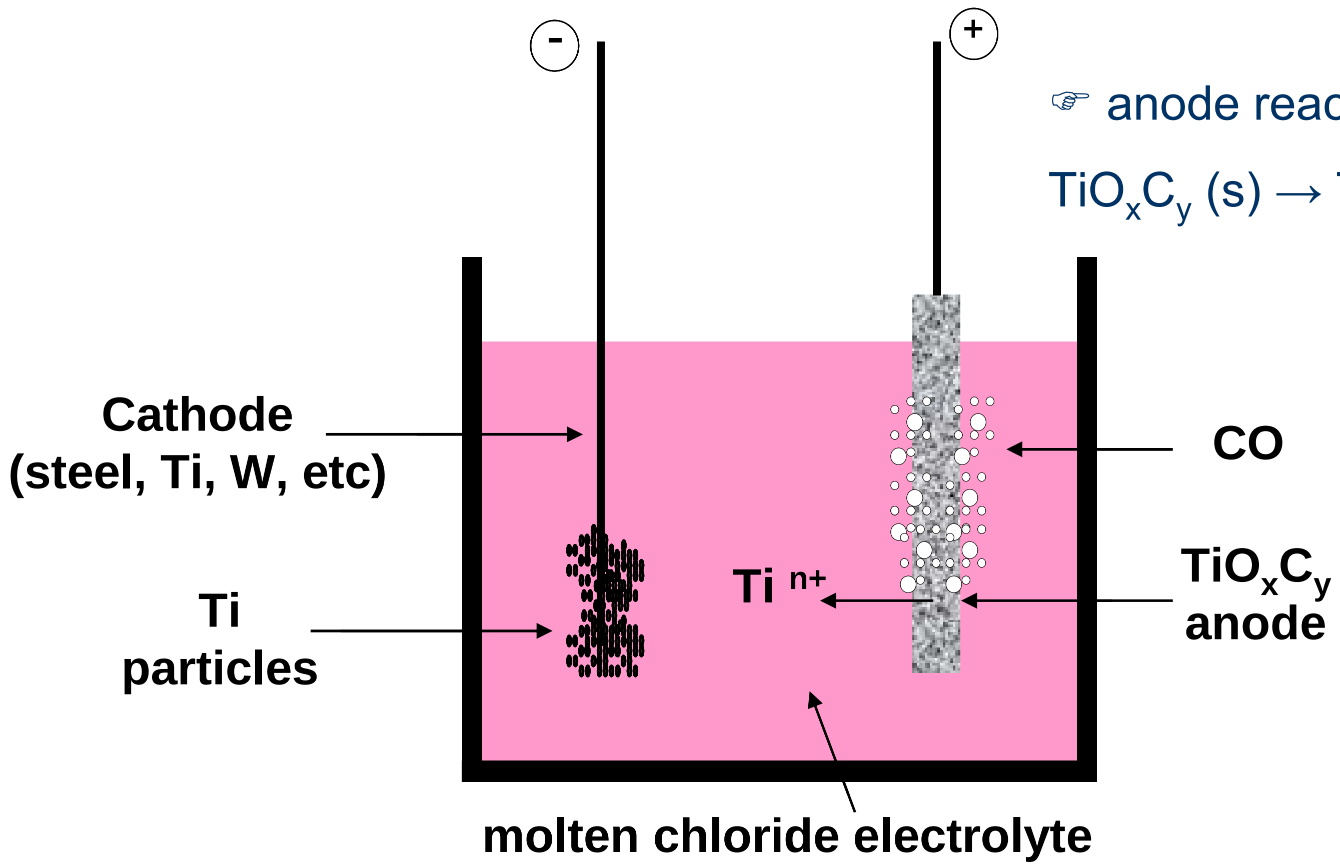
TiO_xC_y anodes

- cathode reaction:

$Ti^{n+} + ne^- \rightarrow Ti\ (s)$

- anode reaction:

$TiO_xC_y\ (s) \rightarrow Ti^{n+} + (x+y)\ CO(g) + ne^-$



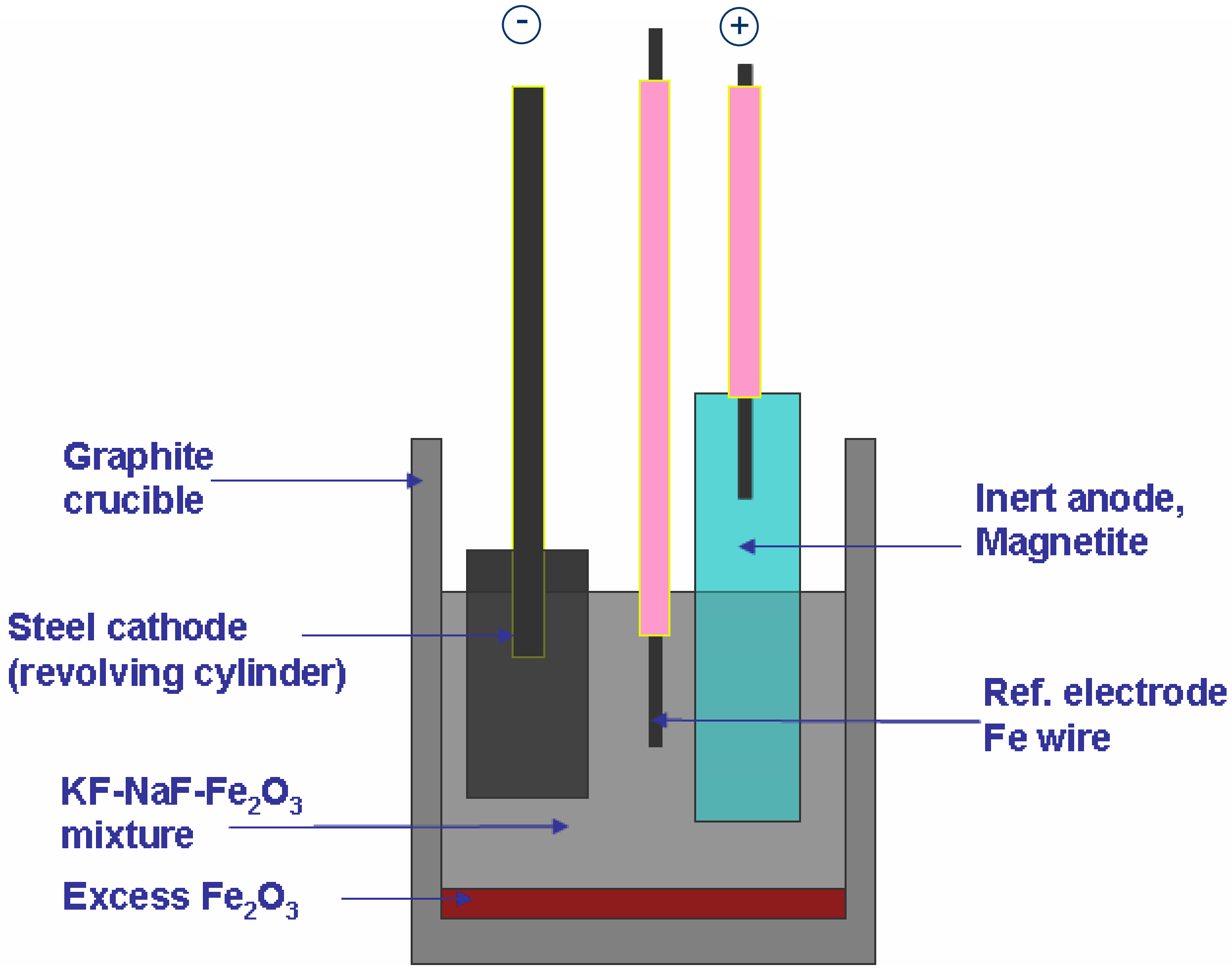
Iron

Fe smelting by carbon reduction of Fe_2O_3 ⟶ CO_2 emission

ULCOS

Ultra Low CO_2 Steelmaking

Iron

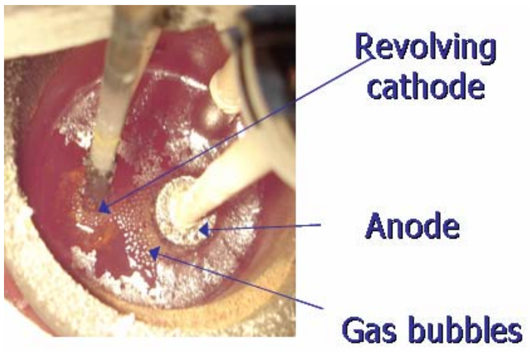


☞ cathode reaction:

$Fe(III) + 3e^- \rightarrow Fe(s)$

☞ anode reaction:

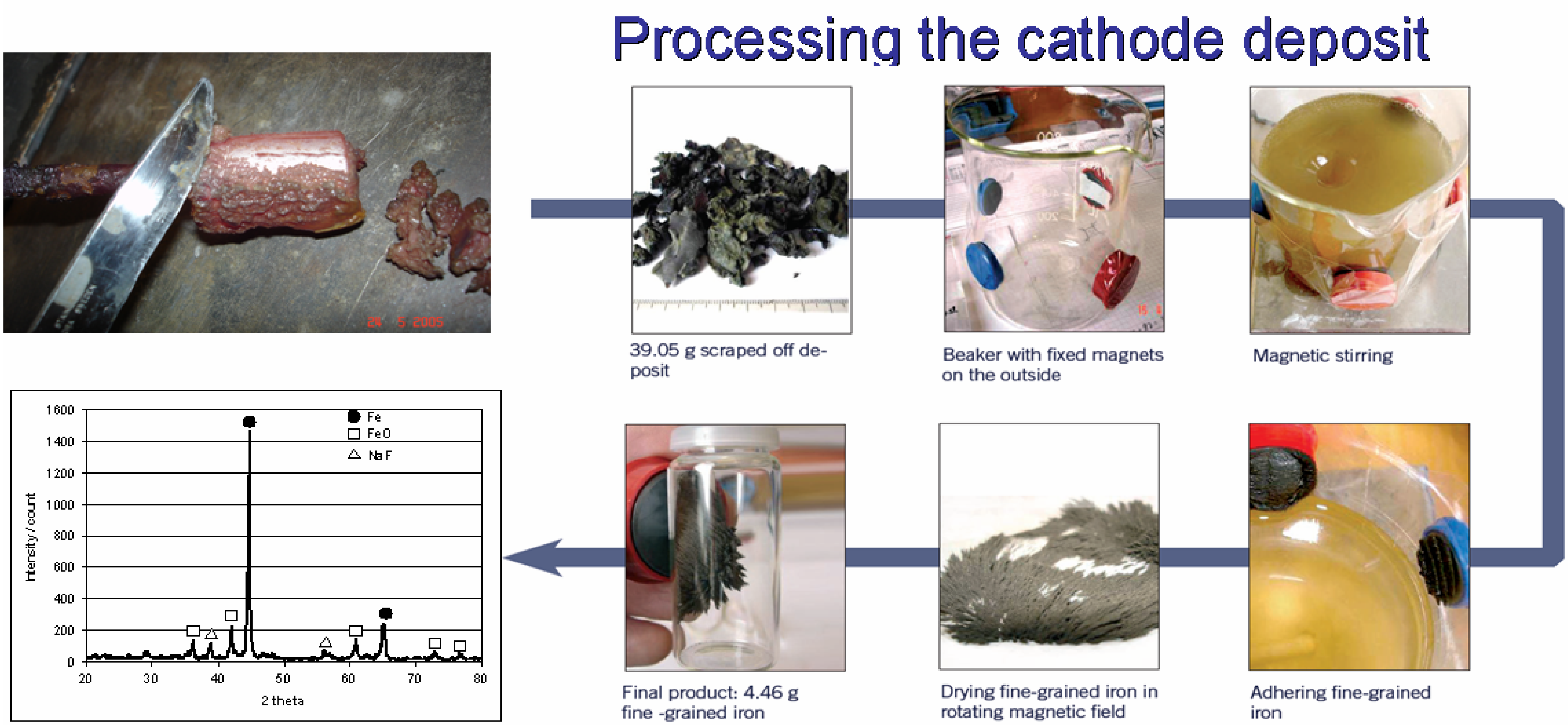
$O^{2-} \rightarrow \frac{1}{2} O_2(g) + 2e^-$




METALSYMBOLS © Metalprices.com

Iron


ULCOS


Processing the cathode deposit
24 5 2005
39.05 g scraped off de-posit
Beaker with fixed magnets on the outside
Magnetic stirring
Adhering fine-grained iron
Drying fine-grained iron in rotating magnetic field
Final product: 4.46 g fine -grained iron
Fe
FeO
NaF
Intensity / count
2 theta
1600
1400
1200
1000
800
600
400
200
0
20
30
40
50
60
70
80

Ionic liquids

Electrolytic processes in room / low temperature molten salts

Ionic Liquids

"Electrodeposition of Si thin-films from Ionic Liquids for Photovoltaic Applications"

Thanks for your attention