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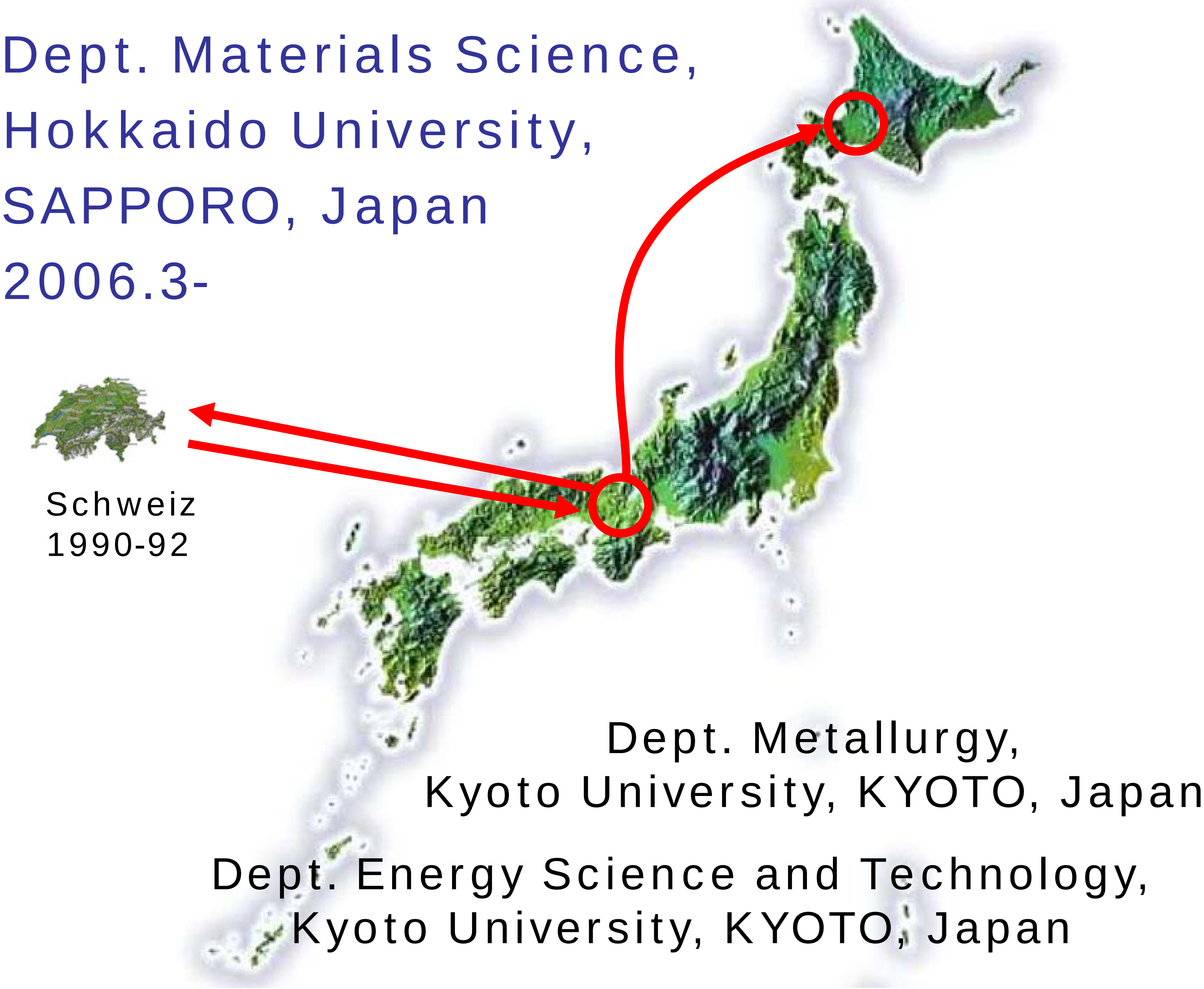
Research Topics

1. High Temperature Thermochemistry for Materials Processing; Ti,Ta,Nb,,,
2. Reactions between Unstable Gases and Materials; Ozone, N*, etc
3. Thermoelectric Power Generation


Dept. Materials Science,
Hokkaido University,
SAPPORO, Japan
2006.3-
Schweiz
1990-92
Dept. Metallurgy,
Kyoto University, KYOTO, Japan
Dept. Energy Science and Technology,
Kyoto University, KYOTO, Japan

Congratulations!

A new international exchange program between *ETH* and Hokkaido Univ. (2007-2011)

New Proposal of Metallic Titanium and its Alloys from TiO_2

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Energy Consumption in Metallurgy

About 100,000,000 ton of Iron (Fe) was produced in Japan in 2007.

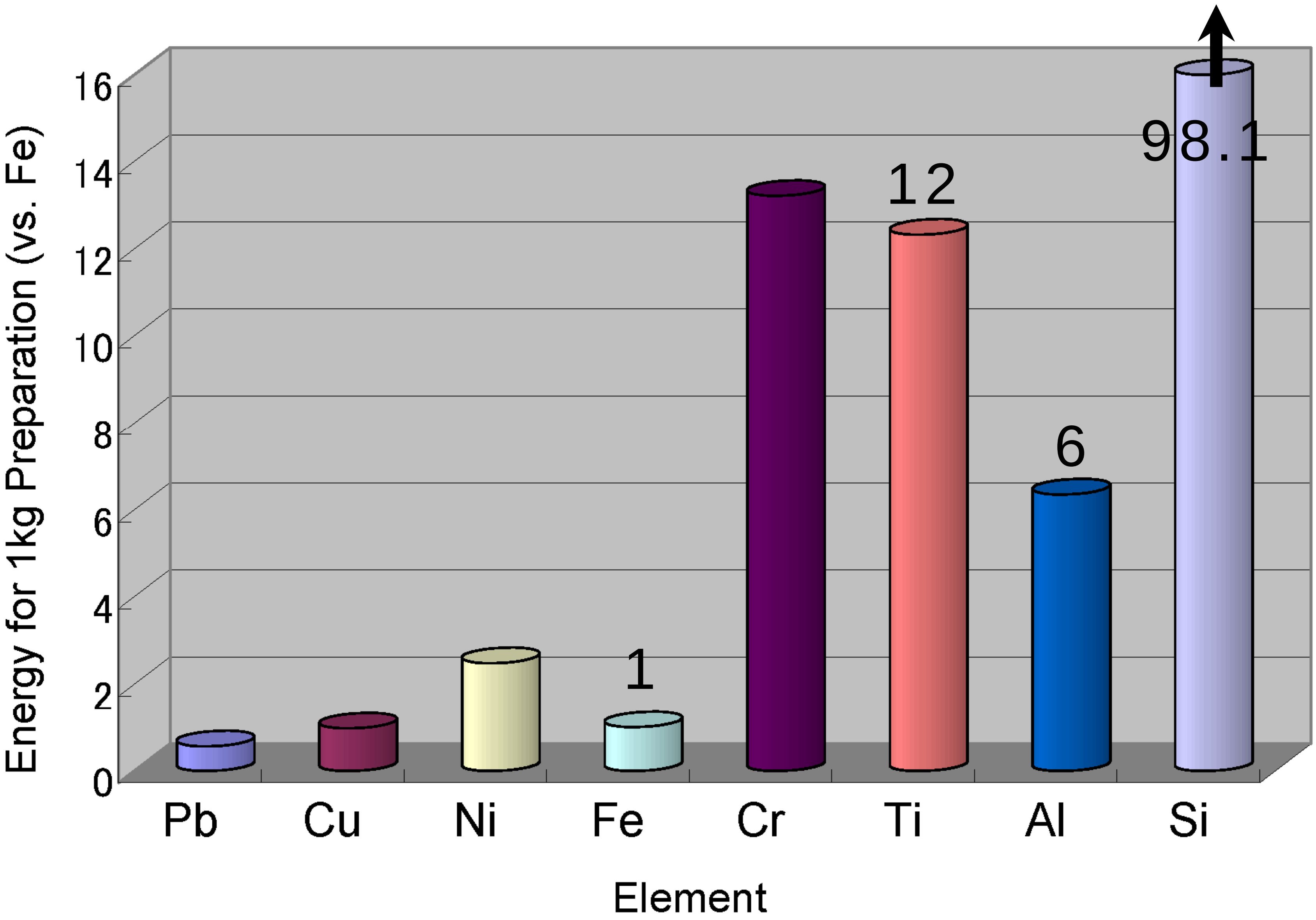
↓

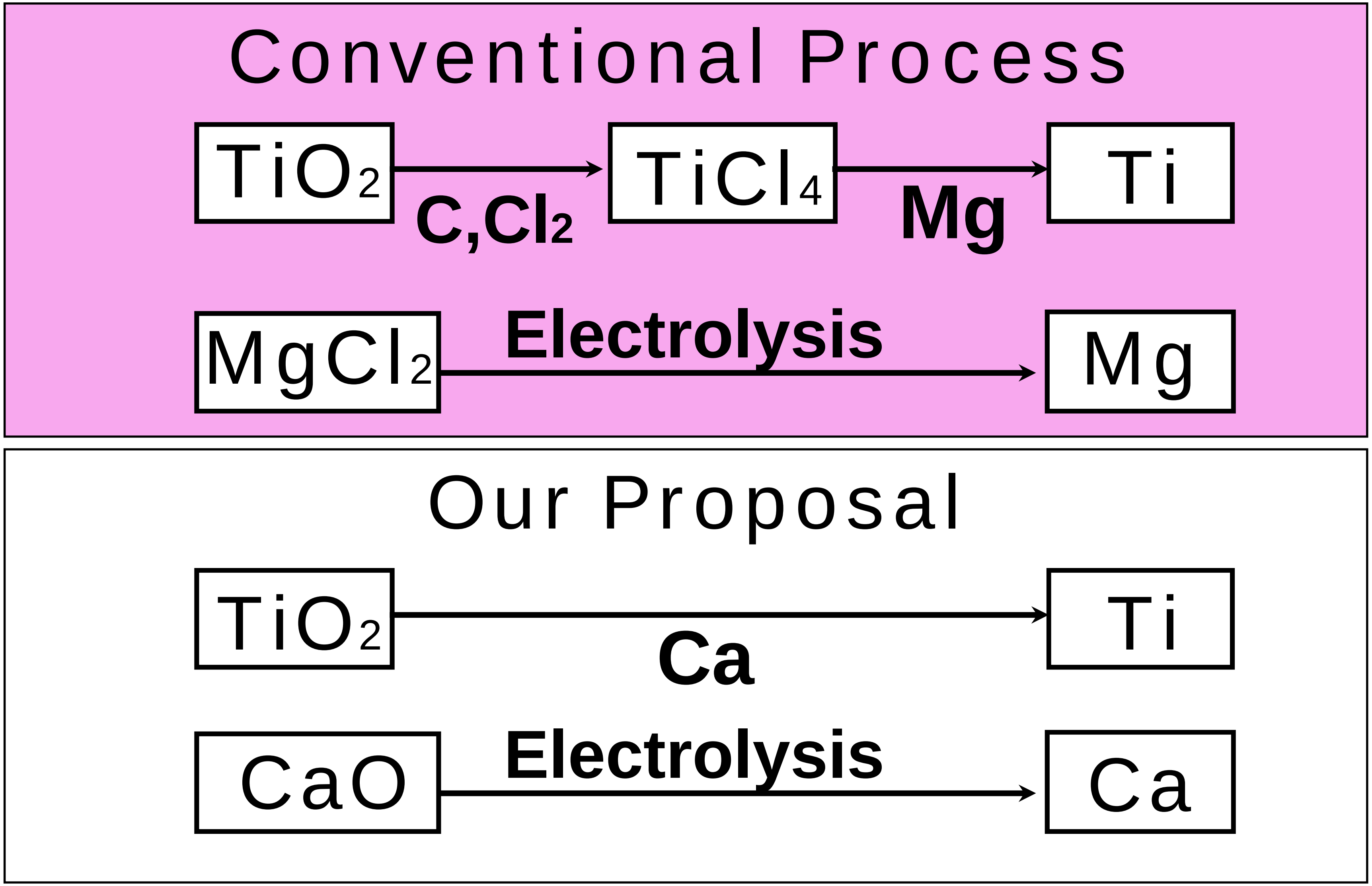
About 950 kg of Fe was produced per a Japanese person annually.

About 480 kg C per 1 ton Fe is needed.

About 500 kg C per 1 ton Al is needed in addition to 1.2 MWH electricity.

Energy Consumption in Metallurgy



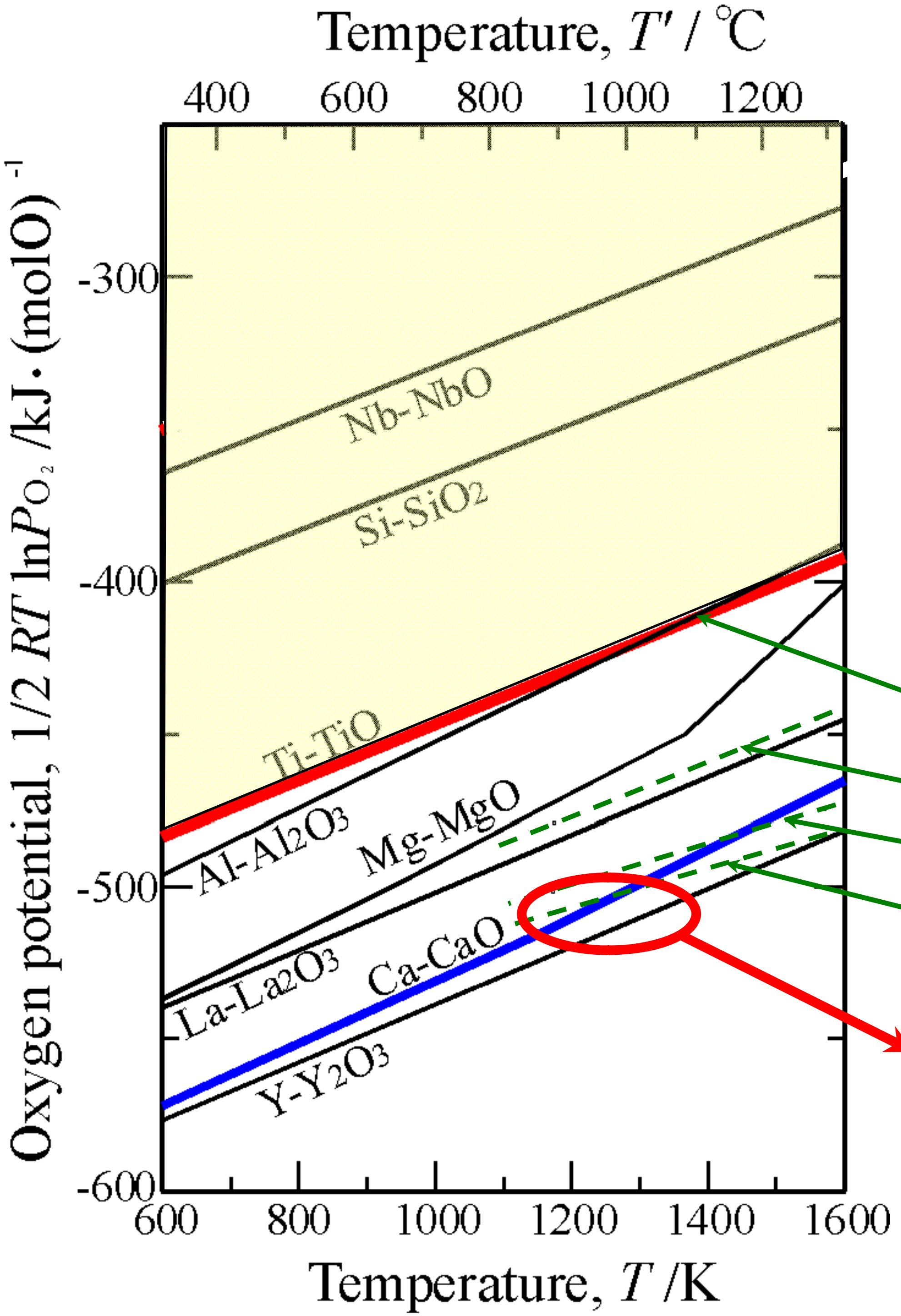


Merits

1. Simple process,
2. Low oxygen content

Why Calcium?

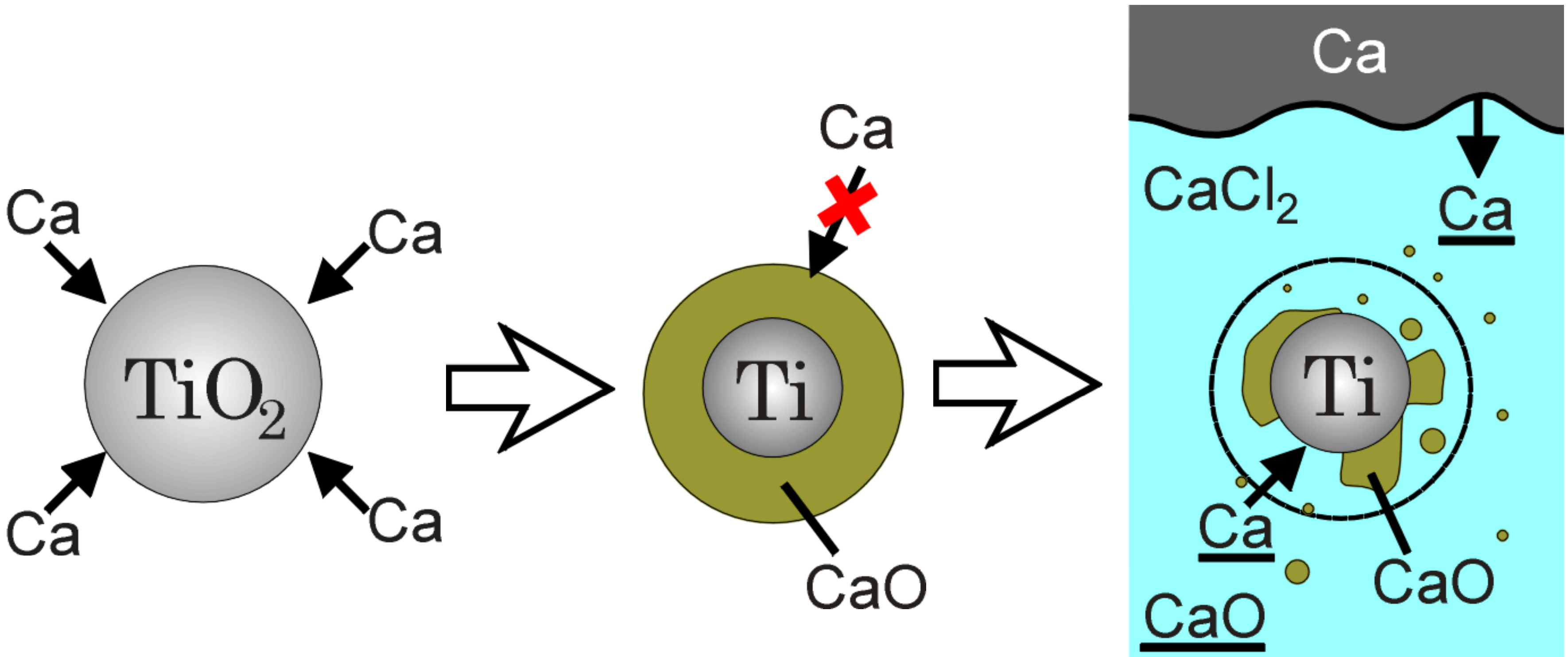
Low oxygen potential
+ Not alloying with Ti.



14mass%O in Ti
1%O
0.5%O
0.1%O

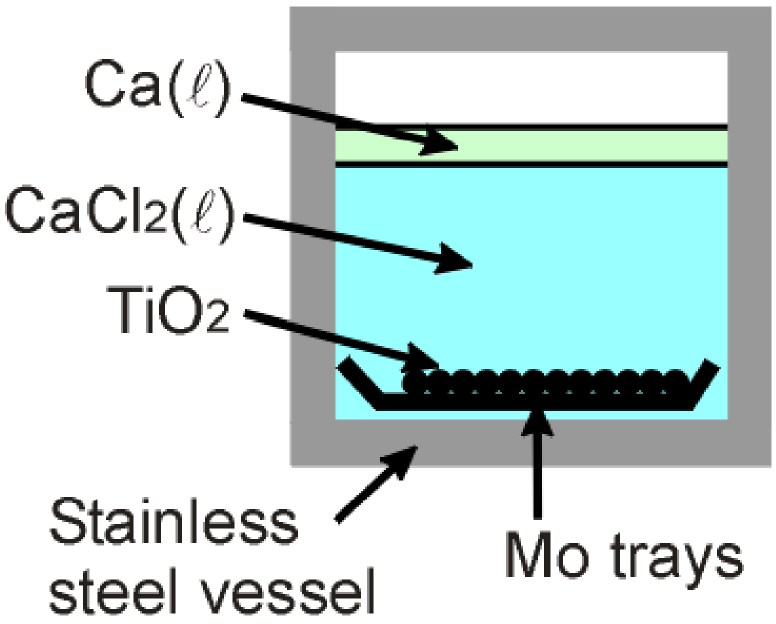
Ca equilibrates with
<1000 ppmO - Ti.

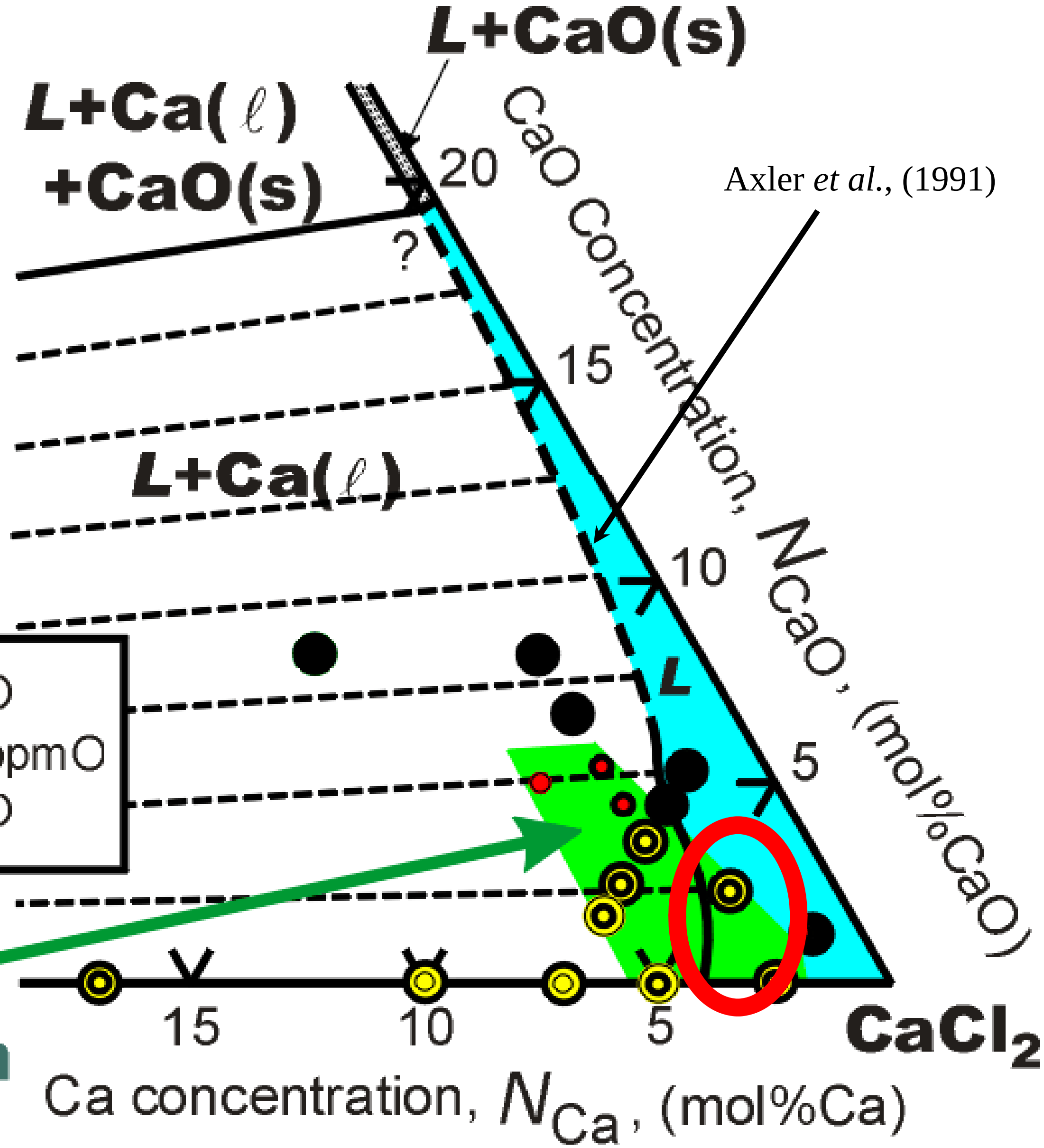
Merit 1. *in situ* CaO removal



$CaCl_2$ can dissolve 20mol%CaO at 1173 K.

Ca reduces TiO_2 quickly even in $CaCl_2$.

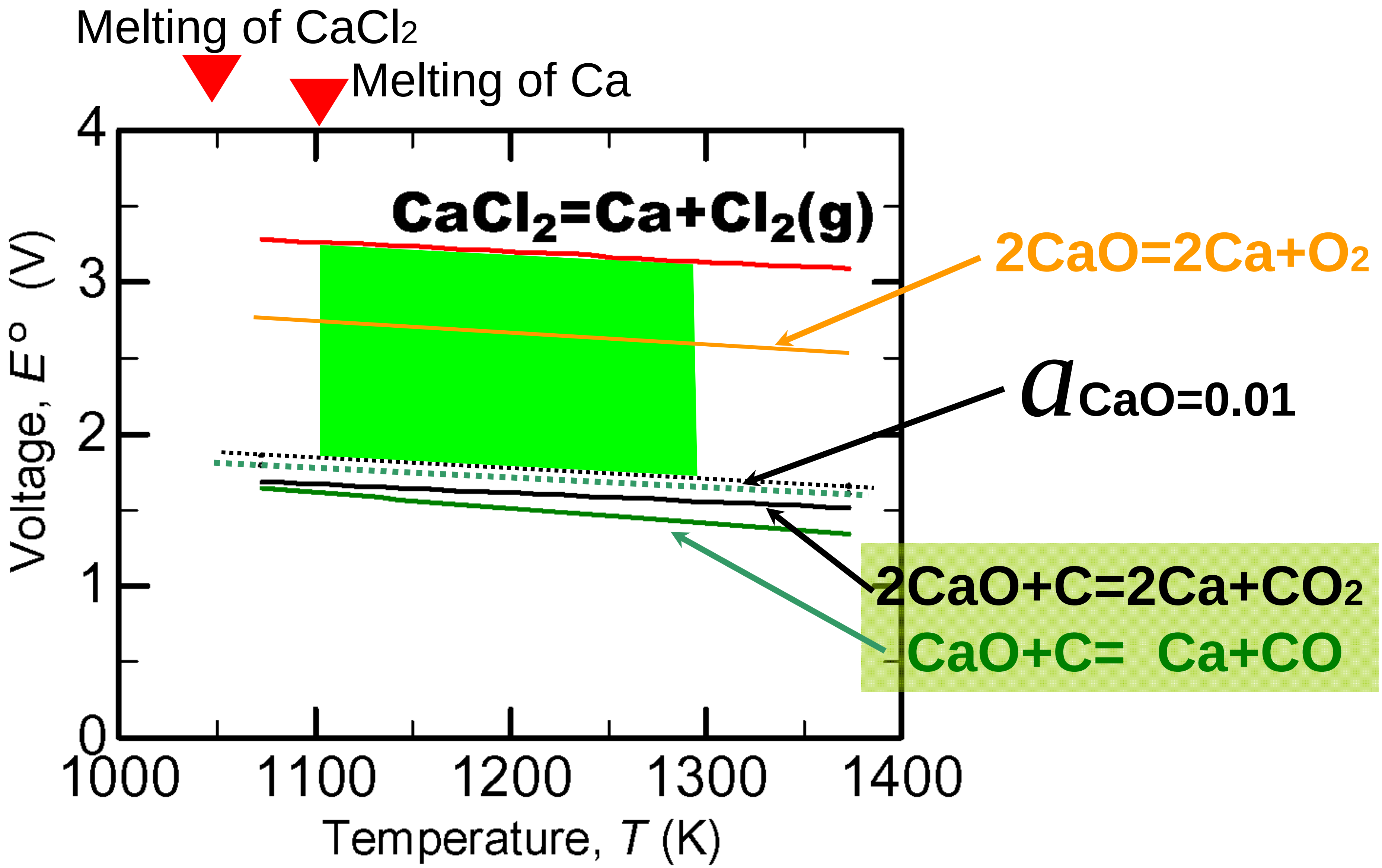


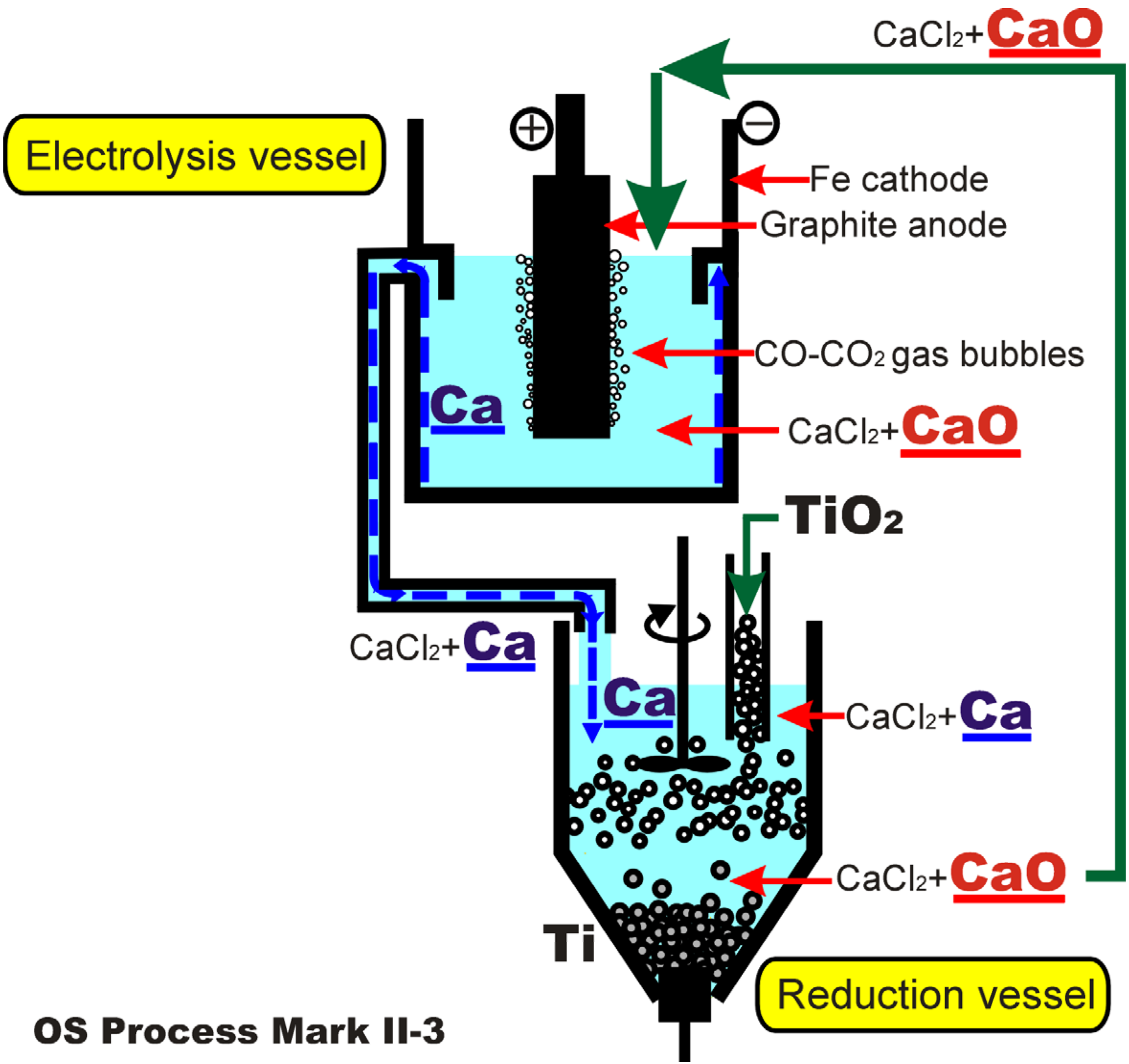


At 1173 K
for 3.6 ks

Bath constituent for single cell operation

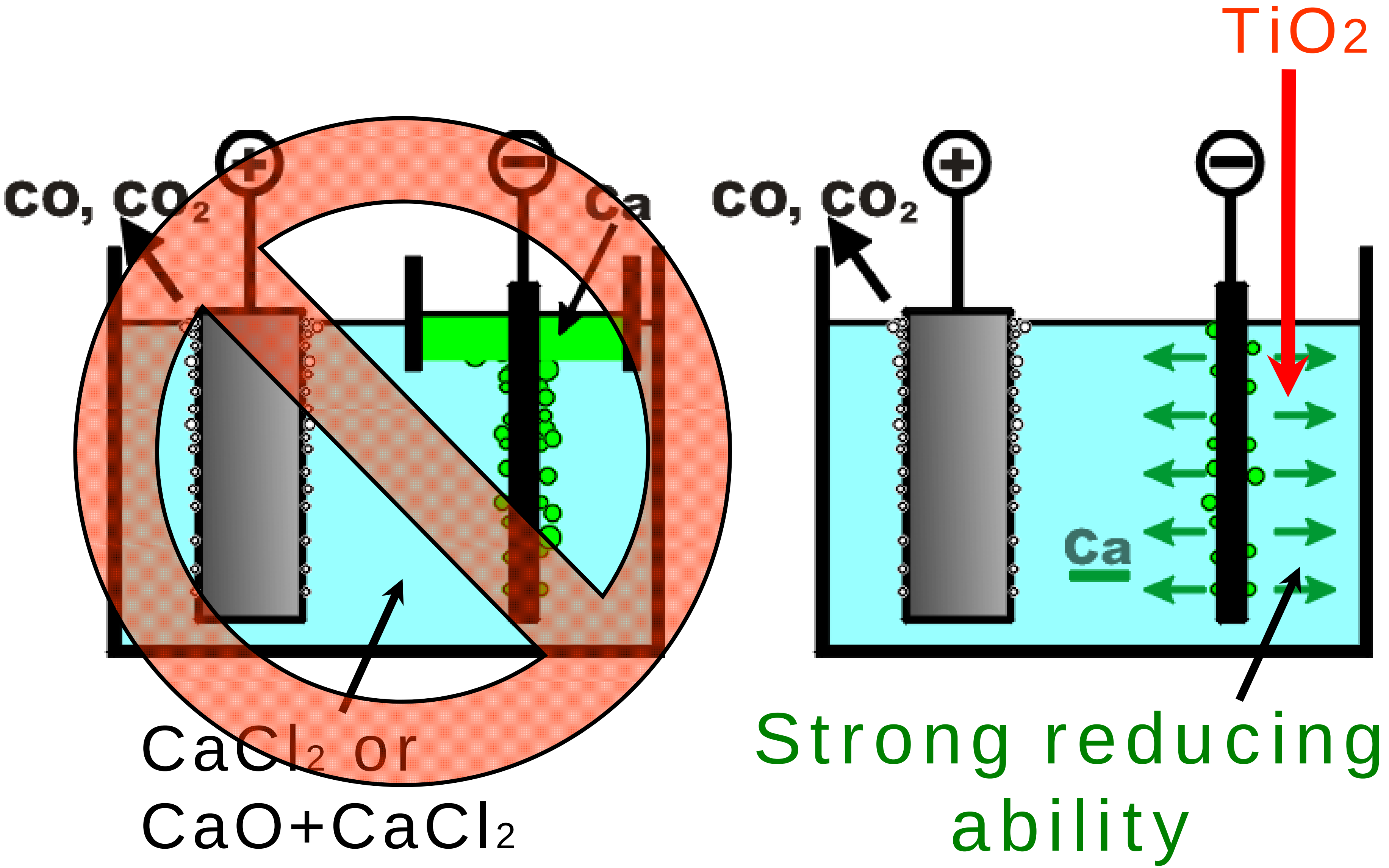
Merit 2. Electrolysis of CaO in $CaCl_2$





OS Process Mark II-3

4mol% Ca dissolves at 1173 K.



OS Process in Single Bath

Electrolysis

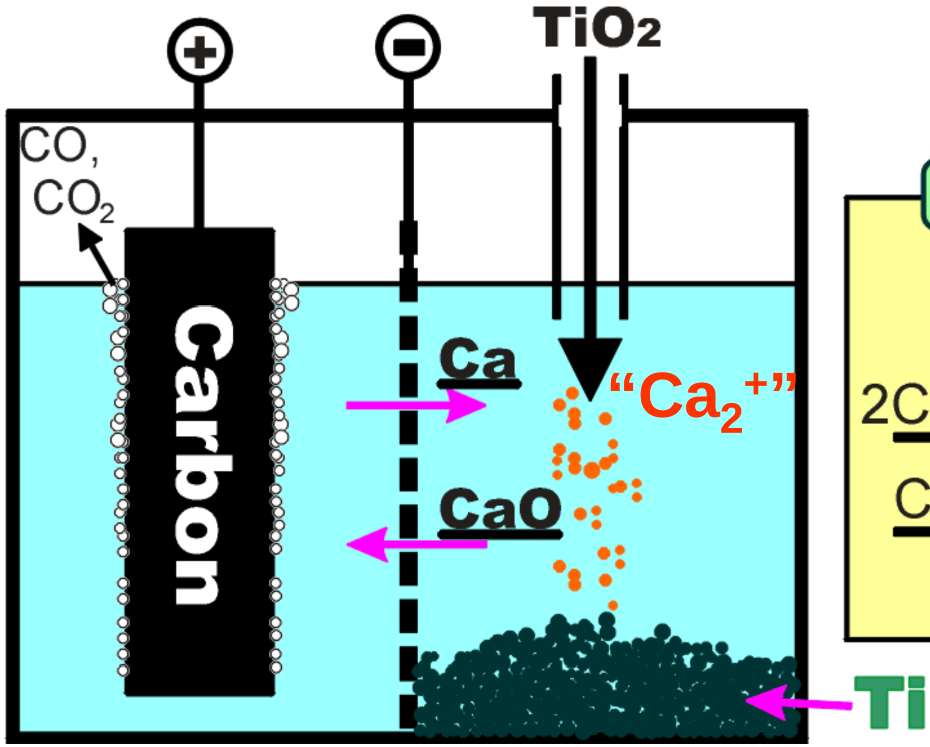
Anode

$2O^{2-} + C = CO_2 + 4e$

$O^{2-} + C = CO + 2e$

Cathode

$Ca^{2+} + 2e = \underline{Ca}$



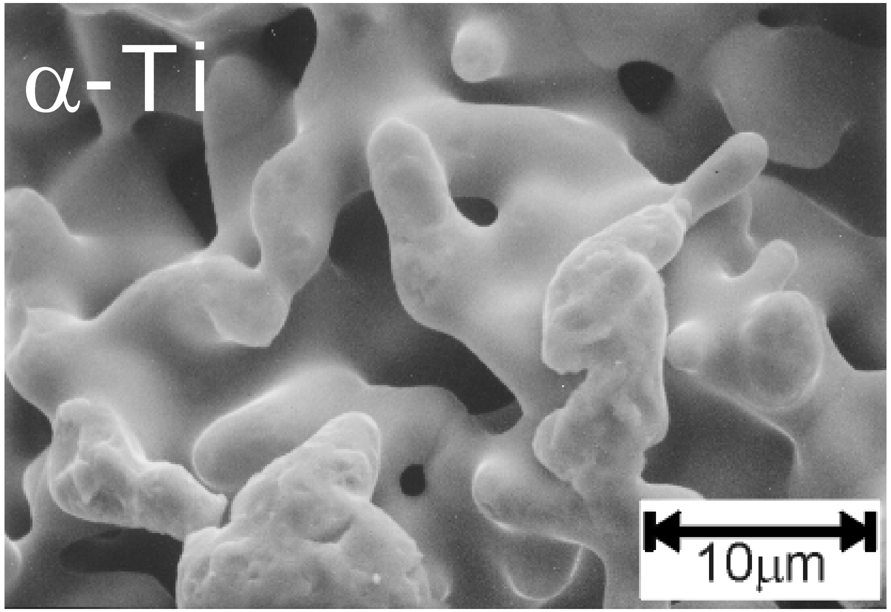
Reduction

$2\underline{Ca} + TiO_2 = Ti + 2\underline{CaO}$

$\underline{Ca} + [O]_{Ti} = \underline{CaO}$

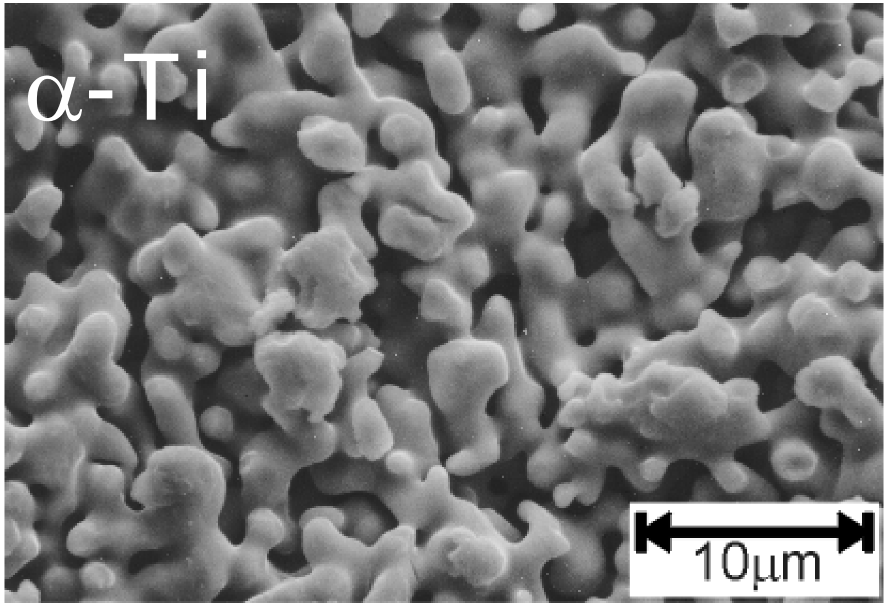
$$TiO_2 + C = Ti + CO_2$$

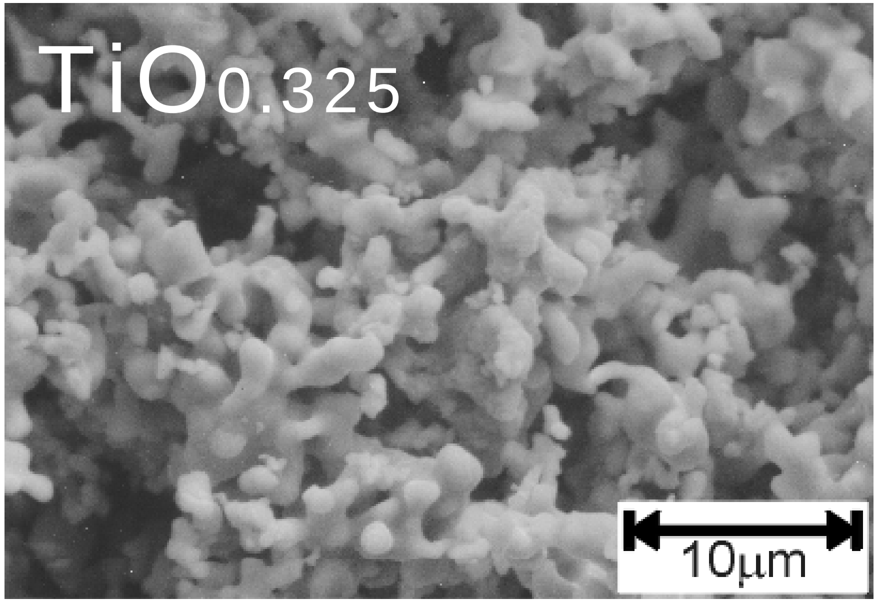
2.7V 0.5mol%CaO



for 10.8ks

2000ppm Oxygen





for 3.6ks

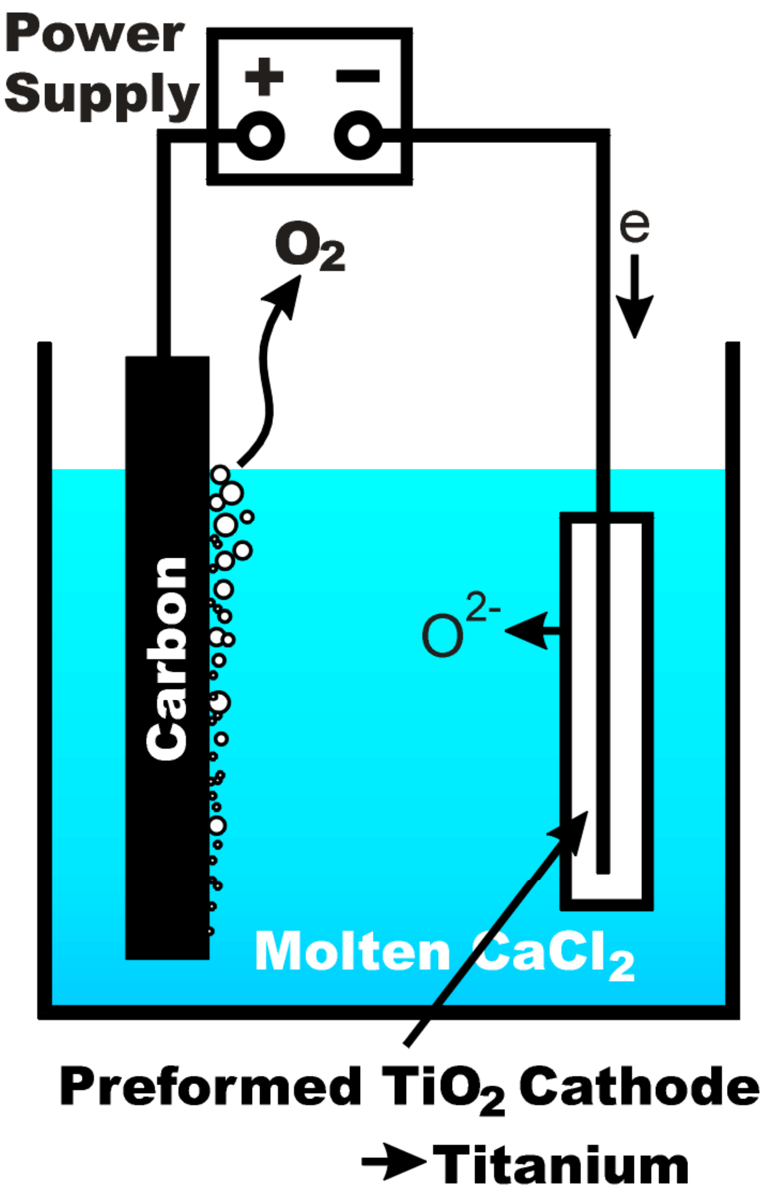

3000kg $CaCl_2$ was filled in.
at Nippon Light Metals, Kambara Works

Results of Other Oxides

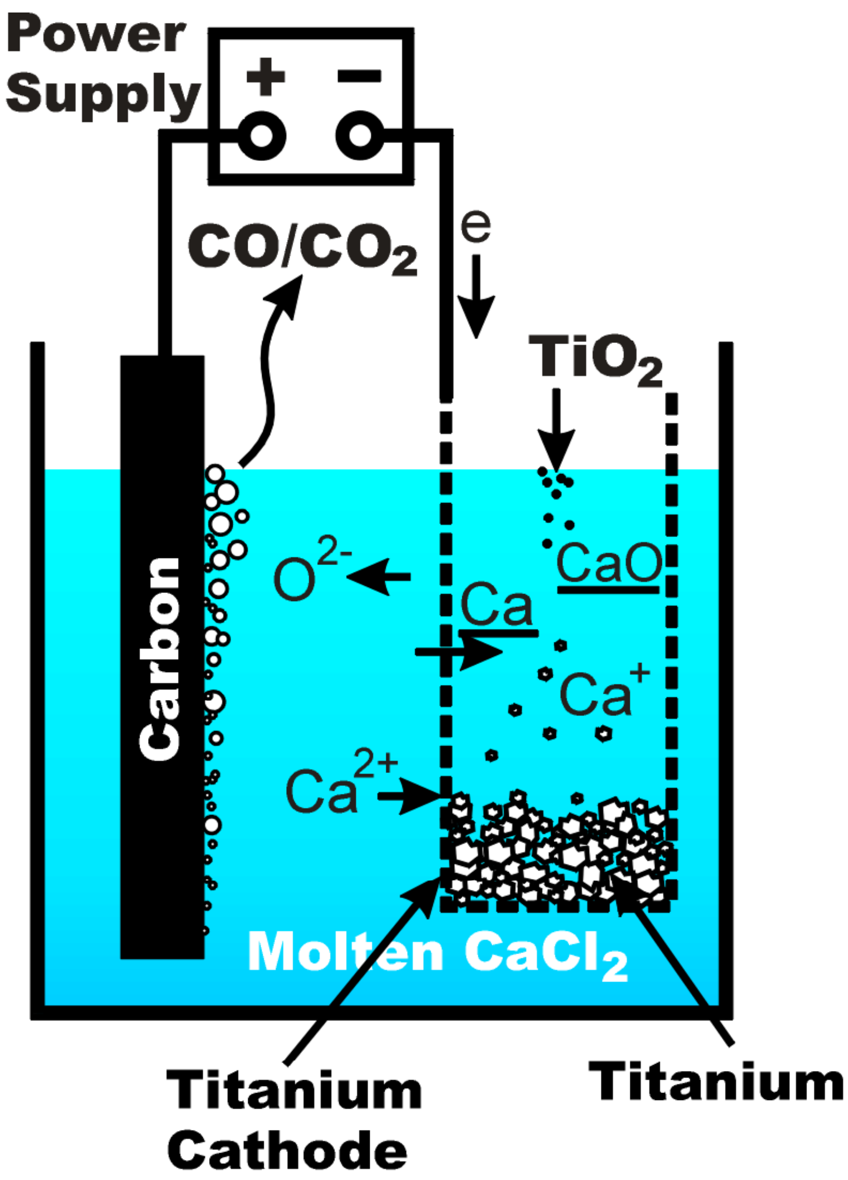
1.0g oxide, 1173K, 1 hour, 3.0V

	Metal	Metal+MC	Metal + Lower oxides	Impossible (still oxide)
Solid Metals	Cr, Fe, Co, Ta, Ni, V	Mo, W	Ti, Zr Nb	–
Liquid Metals	(Ca-Mg), (Ca-Al)	In	Bi, Sn	–
Rare Earth Metals	–	–	–	Y, Er

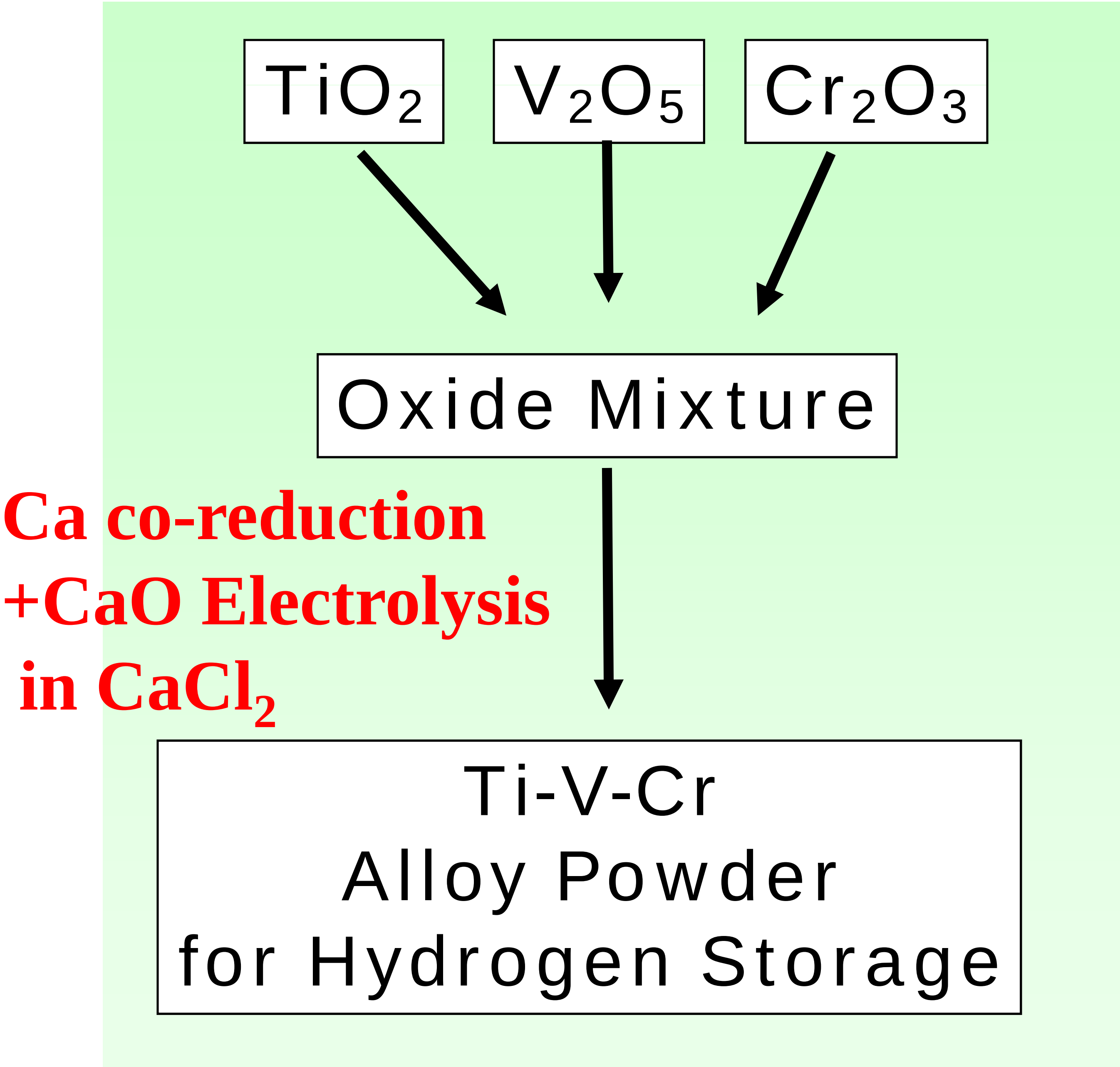
Metals with $\Delta G^0 > 0$ for $MO+Ca=M+CaO$



FFC Process



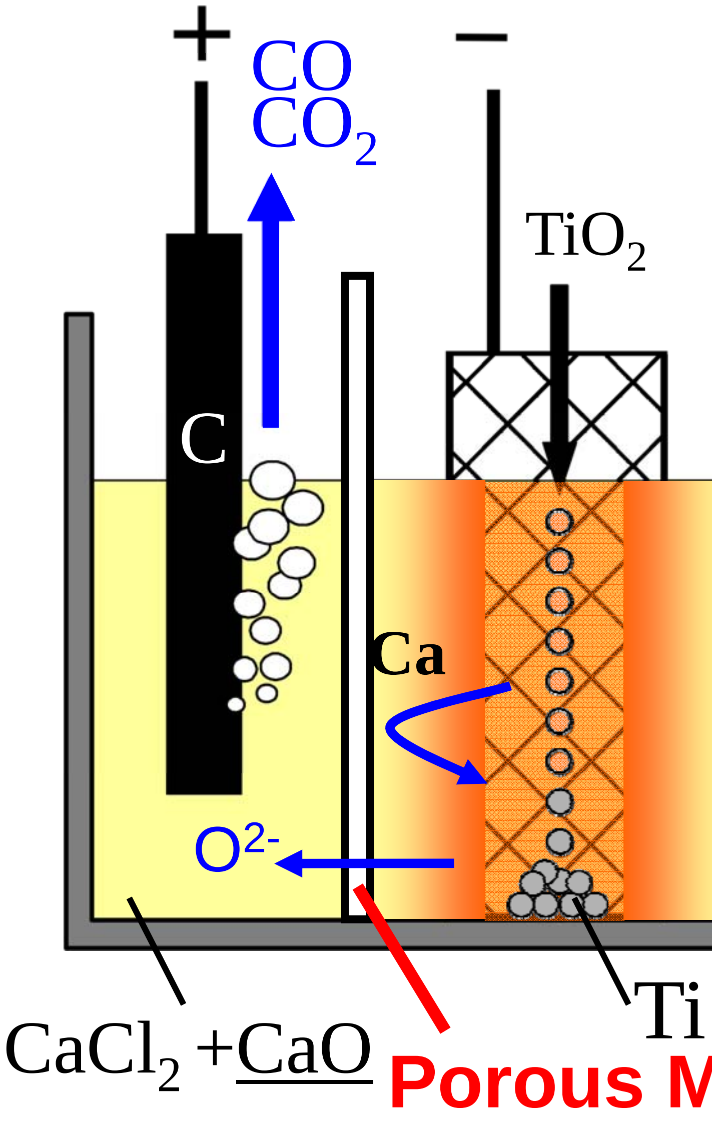
OS Process
(Mark III)



Other Examples

Ti-6Al-4V
Ti-10W
Ti-40V
$TiCr_2$
Ti-Nb
Ti-Fe
Nb_3Sn

Separation of Two Electrodes



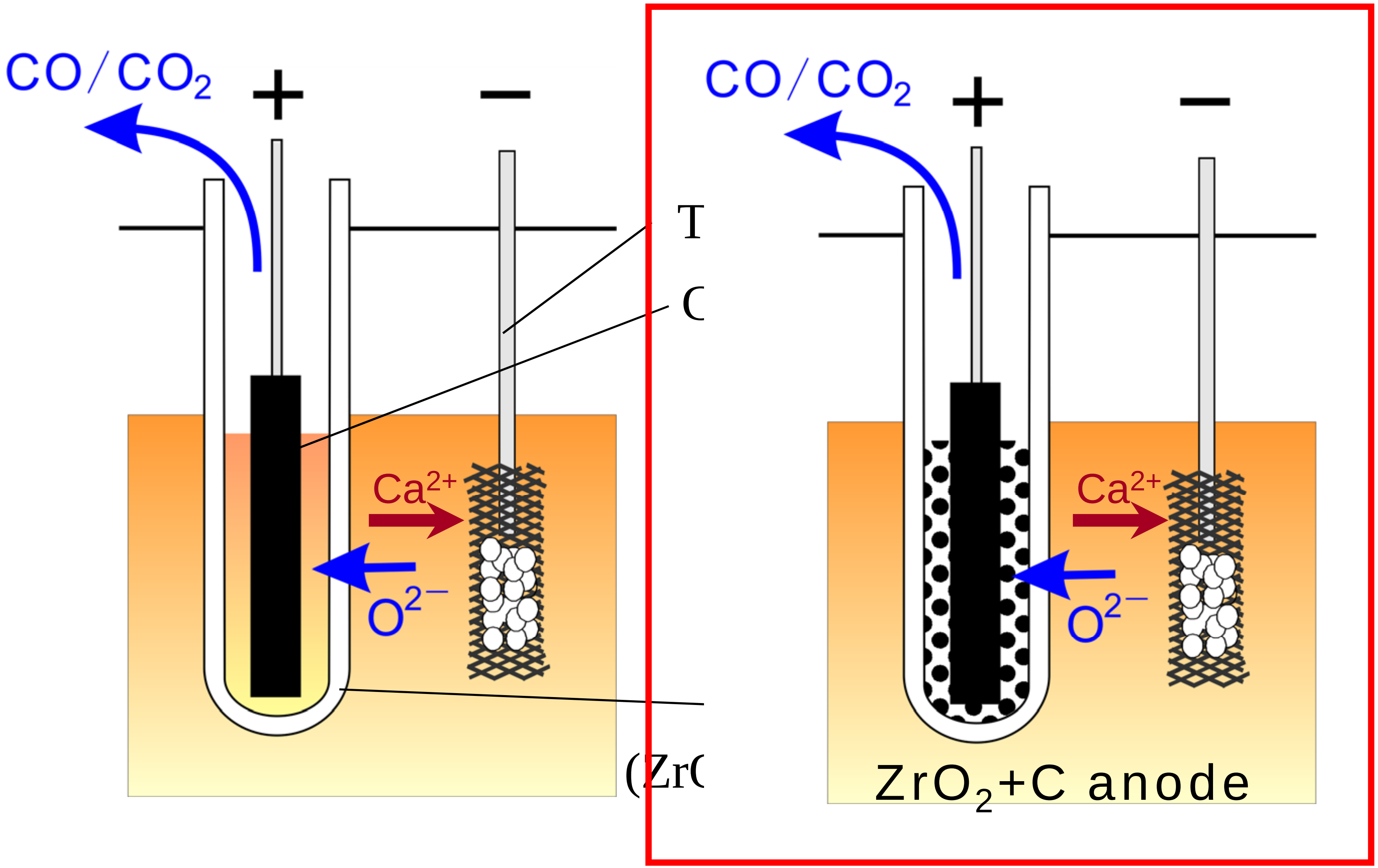
Side Reaction

$CO/CO_2 + Ca = C + CaO$

- Consumption of Ca
  → Lower Current Efficiency
- Carbon contamination of Ti

Yittria Stabilized Zirconia (YSZ) was applied.

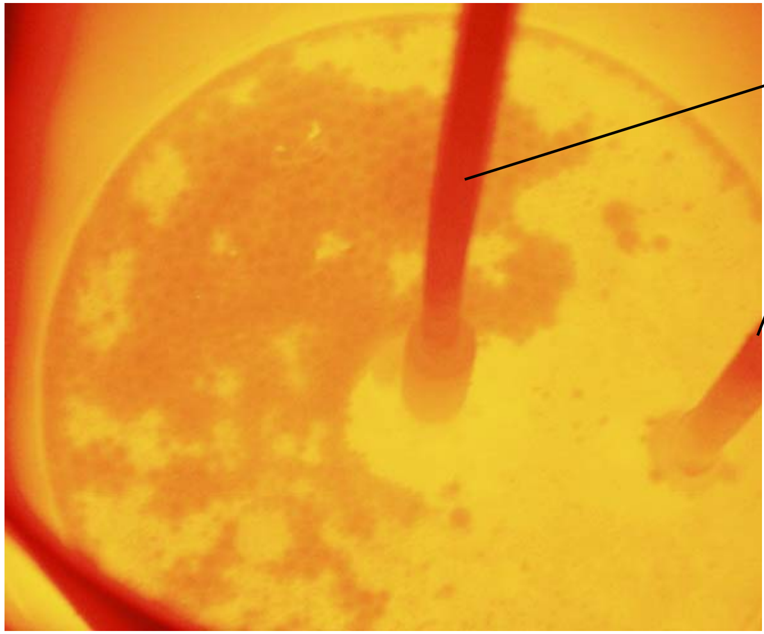
Anode (YSZ + C)



Exp(1): Surface of Molten Salt

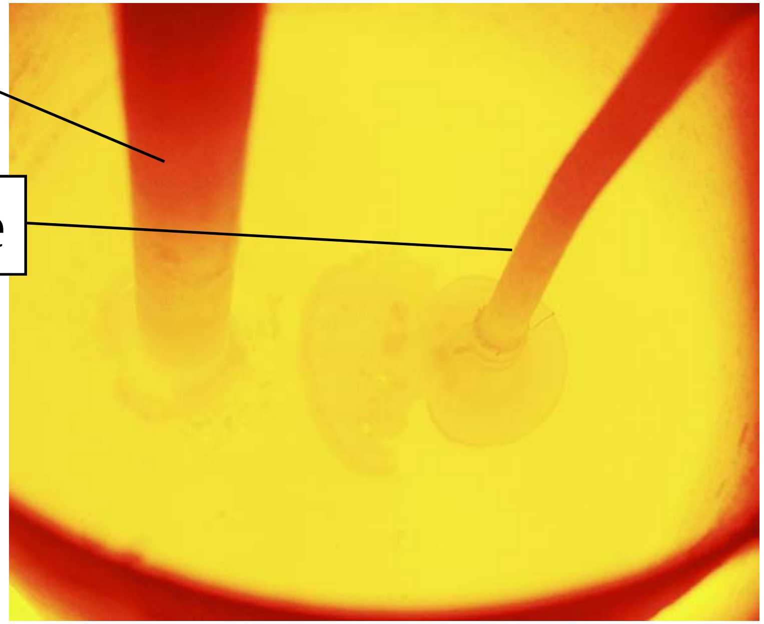
Without YSZ

With YSZ



Anode

Cathode



Around the anode

CO/CO_2 + Ca = C + CaO

CaO + CO_2 = $CaCO_3$

No precipitates

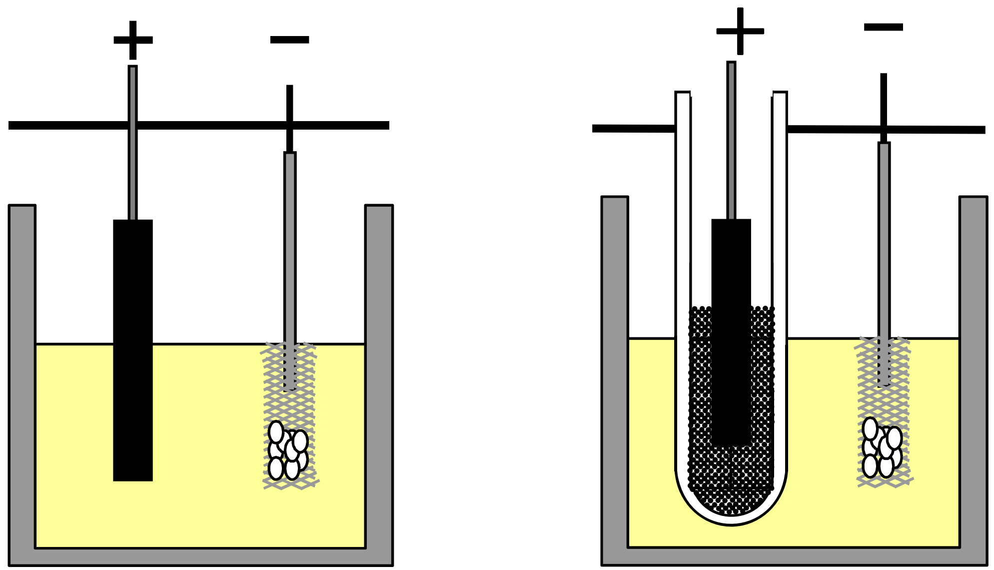
Exp(3): Quality of Ti

C_{CaO}=0.5mol%

3.3V/hr+6hr

Q=20000 C

TiO_2 1.0g



With C

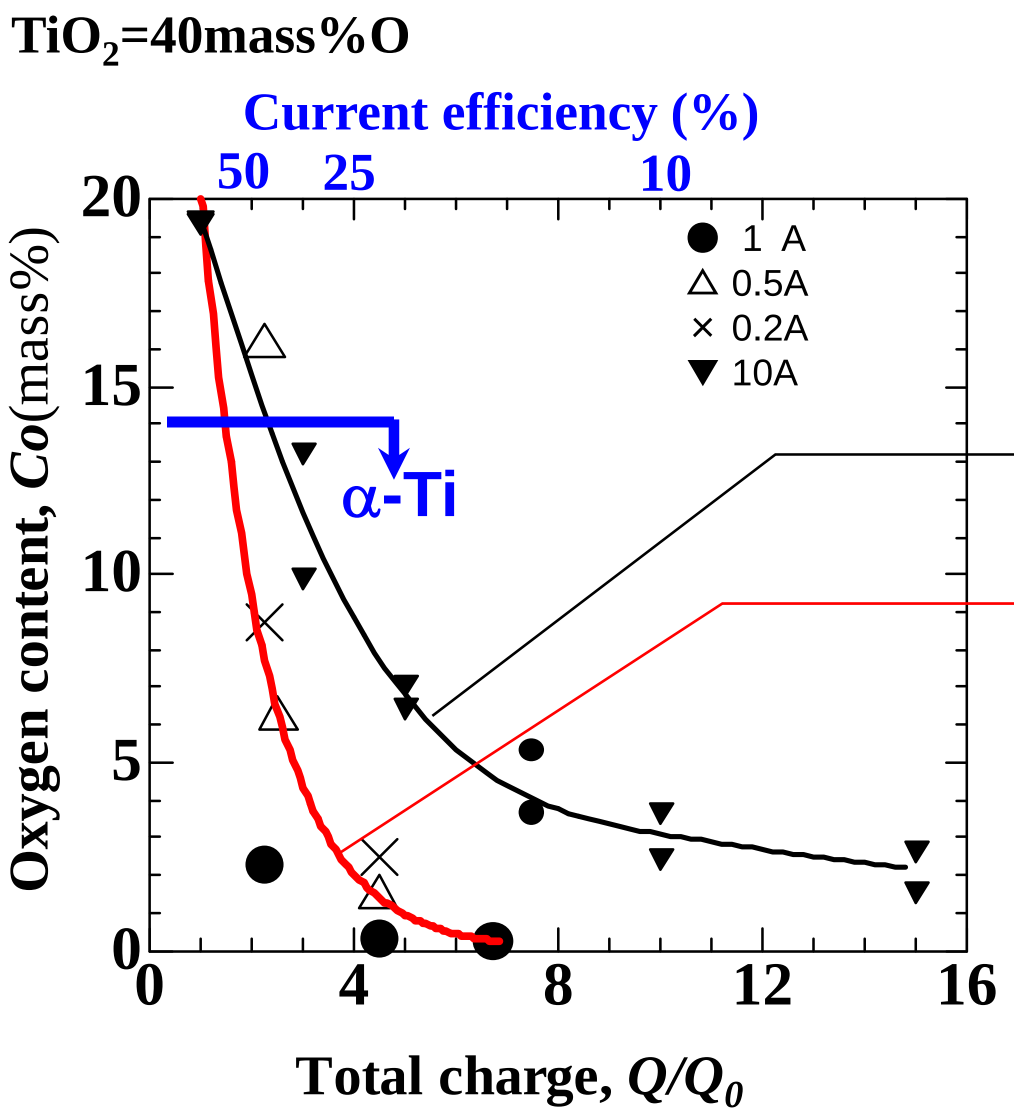
With YSZ+C

	With C		With YSZ+C
Oxygen	5.5%	→	1400 ppm
Carbon	2600 ppm	→	300 ppm

Lower than JIS(TS-140)

Effective separation of CO/CO_2

Exp(4): Current Efficiency



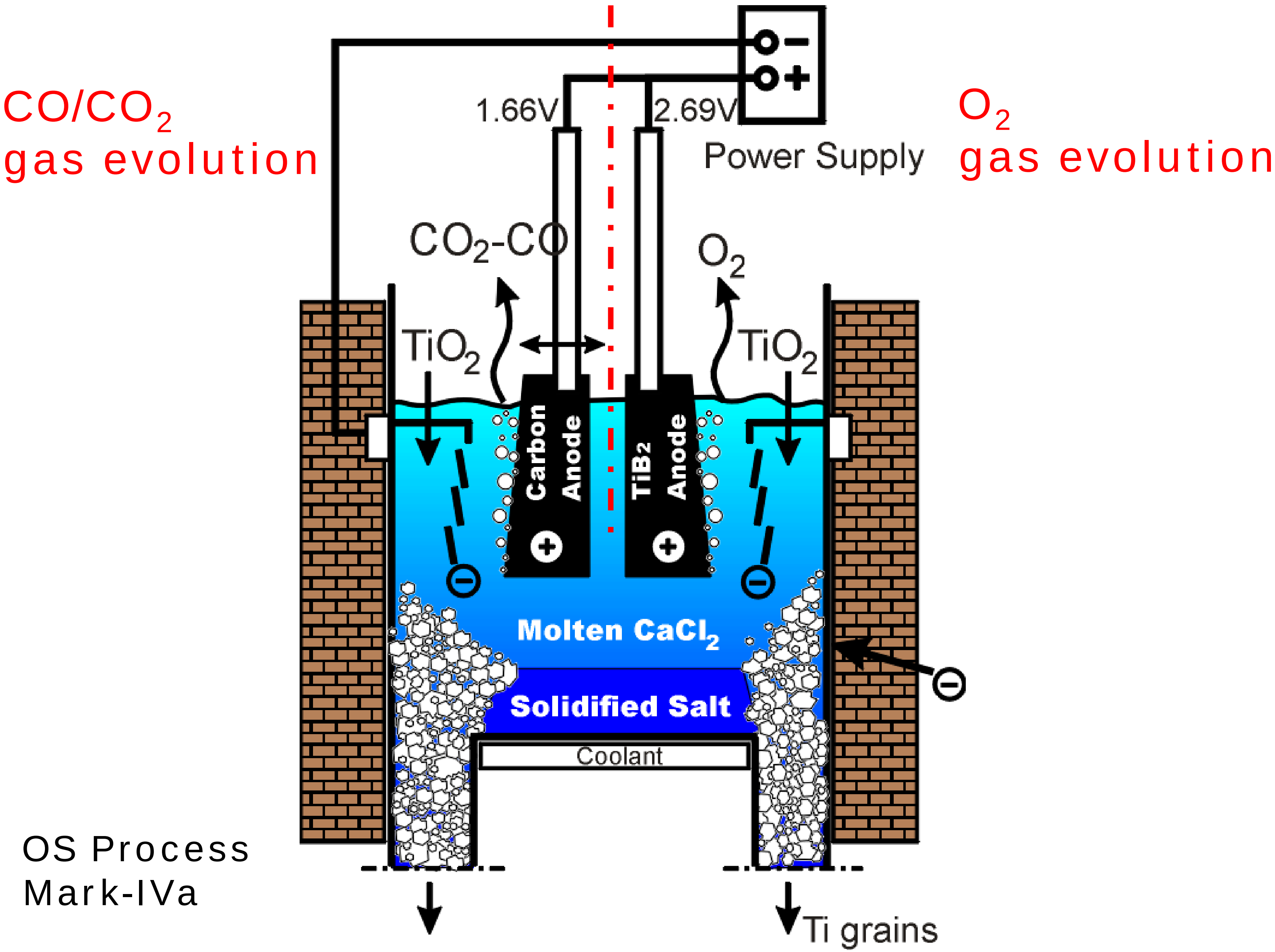
Q_0: Theoretical charge to reduce 1 g TiO_2 (=4825 C)

Q: Supplied charge

Without YSZ

With YSZ

Improved by New Anode (YSZ+C)



CO/CO$_2$
gas evolution
1.66V
2.69V
Power Supply
O_2
gas evolution
CO_2-CO
O_2
TiO_2
TiO_2
Carbon Anode
TiB_2 Anode
Molten $CaCl_2$
Solidified Salt
Coolant
OS Process
Mark-IVa
Ti grains

Conclusion

TiO_2 and the other oxides are successfully reduced by the dissolved Ca from CaO.

(1.6 V < *E* < 3.2 V)

1. Oxide mixture was directly converted to the metallic alloys.
2. New anode (ZrO_2 + C) could eliminate C contamination in Ti.

(1.6 V < *E* < 2.25 V)


Thank you
for your attention.