Tetsuya Uda

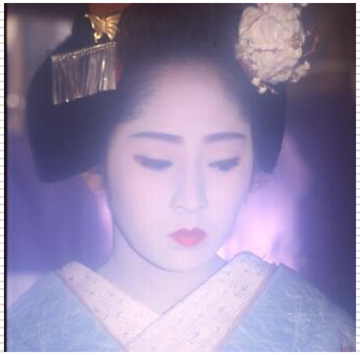
Associate Professor

Materials Science & Engineering

Kyoto University

City of Kyoto

Ancient capital for about 700 years. The most famous city for Sightseeing in Japan.



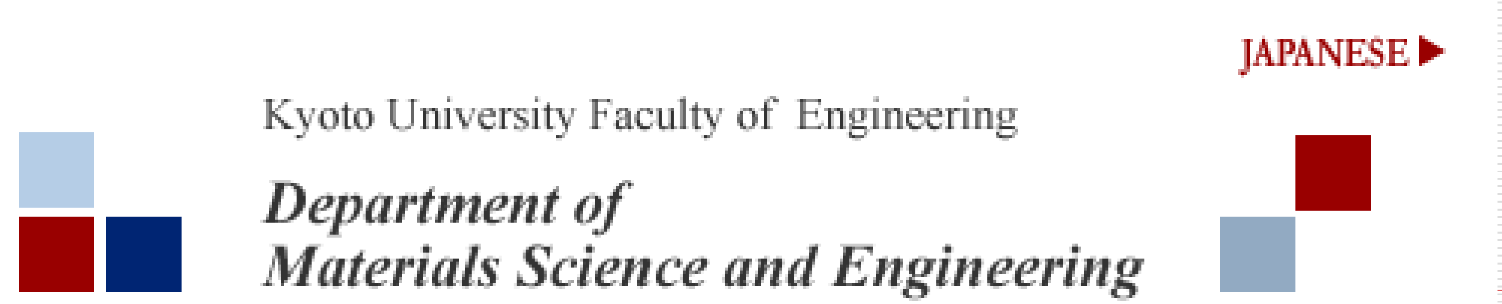
Kyoto University

- Professors 2911
- Undergraduate 13064
- Graduate students 9578

- Strong history in basic science
- Six Nobel winners

Materials Science & Engineering

- Small department, 10 laboratories
- 37 graduate student per grade
- 55 undergraduate student per grade
- About 10 % of graduate student goes to doctoral course
- Each laboratory consists of
  one professor,
  one associate professor
  one assistant professor
  three to four graduate students
  six undergraduate students



JAPANESE ▶

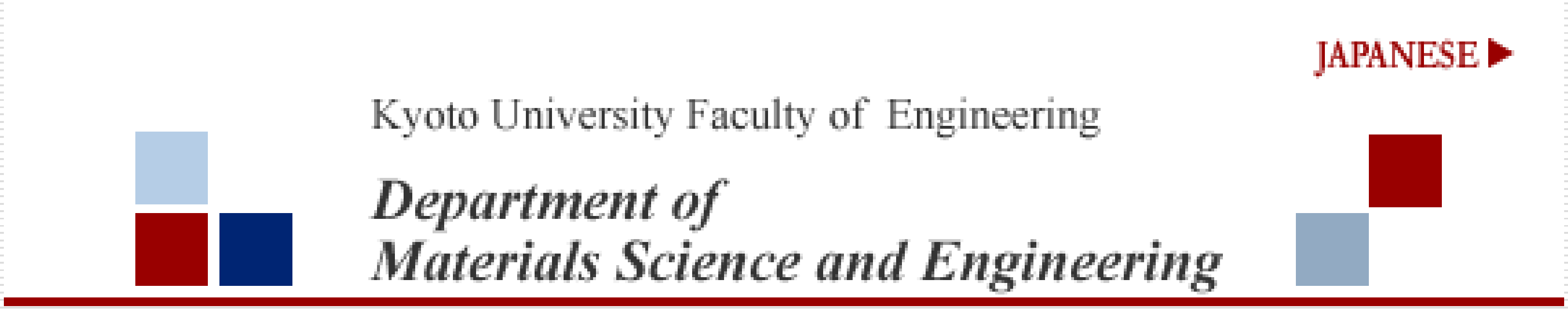
Kyoto University Faculty of Engineering

Department of
Materials Science and Engineering

Aluminus of the department

Undergraduate 1988
Ph.D. 1993

The most famous professor in metallurgical processing including titanium deoxidation, rare metal processing, various recylcing process & alcohol science in Japan.



JAPANESE ▶

Kyoto University Faculty of Engineering

Department of
Materials Science and Engineering

Tetsuya Uda

Undergraduate, Kyoto University, 1994
Master course, Kyoto University, 1996

"A basic study of reduction process of titanium chlorides"

under supervisor of Profs. Okabe and Waseda.
Ph.D. Tohoku Univeristy, 1999

Served as

1999–2002	Research Associate, Tohoku University
2002–2005	Postdoc, California Institute of Technology Sossina M. Haile lab
2003–2005	Proton Power Inc.(Superprotonic, Inc.,) CTO
2005–2006	Assistant Professor, Kyoto University
2006–	Associate Professor, Kyoto University

Research History/Current Research

1 "A basic study of reduction process of titanium chlorides"
under supervisor of T.H.Okabe and Y.Waseda

2 "Recycling process of rare earth sludge and rare earth separating technology"

3 "Solid Acid Fuel Cell" *Active*
with Prof. S.M.Haile, Drs. D.Boysen and C. Chisholm

4 "Development of proton conductive oxide" *Active*

5 "Electroplating titanium in room temperature molten salt" *Active*

with Profs. K.Murase and Y.Awakura

6 "Reduction of titanium compounds" *Active*

with Prof. Y.Awakura

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Rare Earth Magnet

~ The strongest magnet in the world~

http://www.shinetsu.co.jp/

Basic Composition :

$Nd_2Fe_{14}B$

- The highest performance

$SmCo_5$ or Sm_2Co_{17}

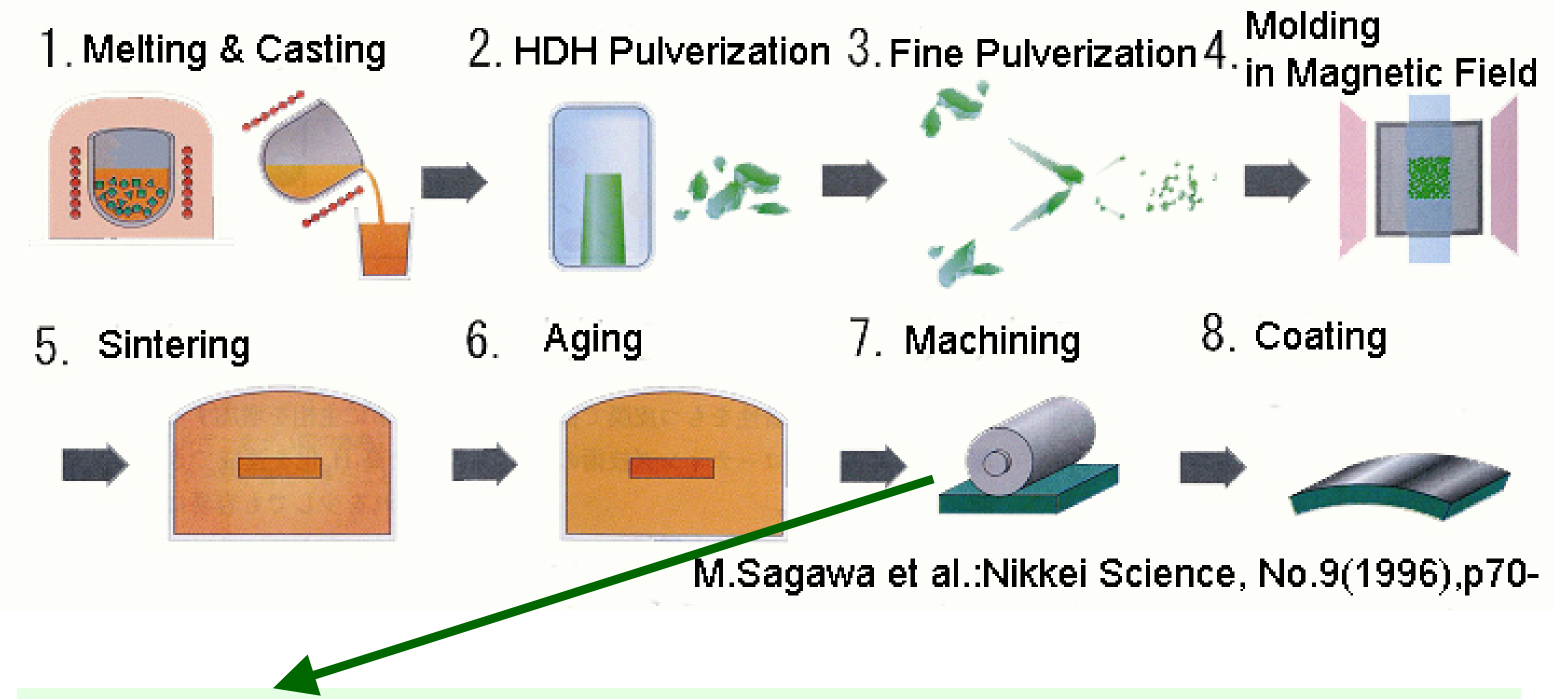
- Excellent in thermal properties & corrosion resistance

Application:

- **Hard disk drive**
- **High energy-efficient motor**

Manufacture Process for Sintered Rare Earth Magnet

Nd-Fe-B Sintered Magnet



1. Melting & Casting
2. HDH Pulverization
3. Fine Pulverization
4. Molding in Magnetic Field
5. Sintering
6. Aging
7. Machining
8. Coating

M.Sagawa et al.:Nikkei Science, No.9(1996),p70-

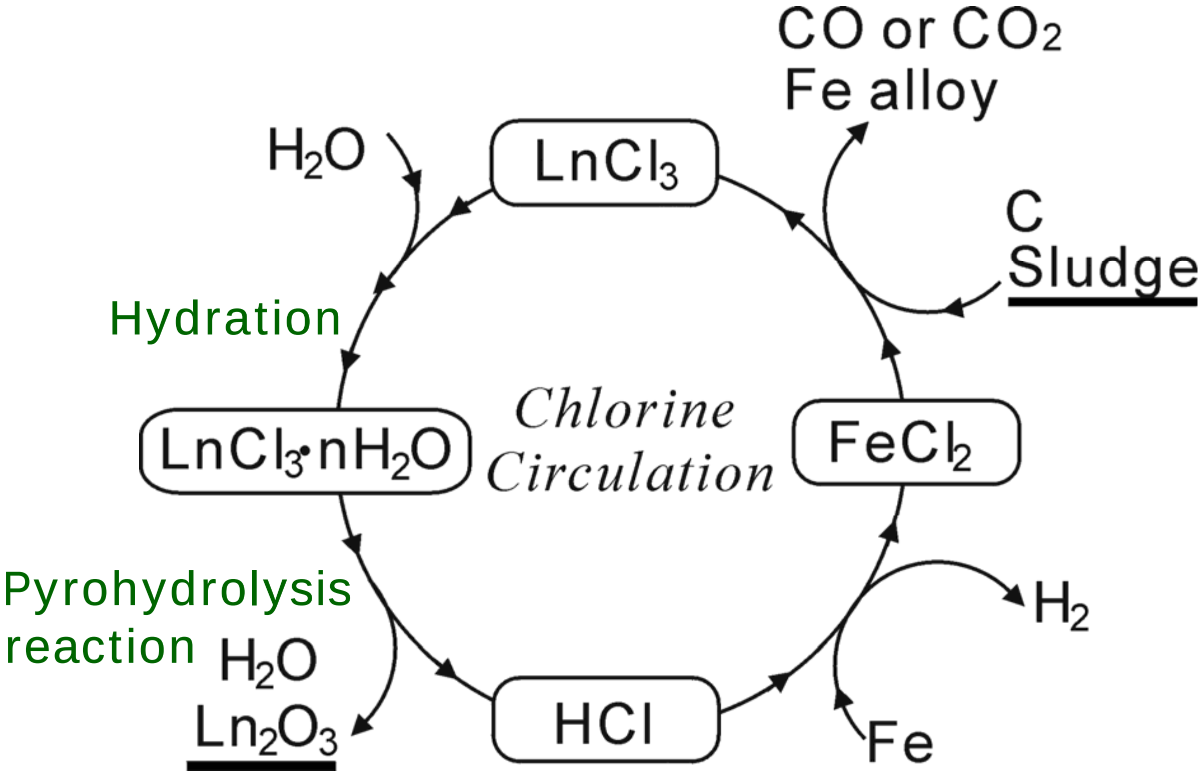
Sludge (Grinding & Machining Waste)
→ Several Tens Percent of Raw Materials
(typically 50 %)

It is very important to reuse this sludge.

However…..

- The sludge is considerably contaminated by oxygen, it is difficult to reuse it as it is.
- Thus, establishment of efficient recovery method of rare earth is needed.

Propose new recycling process



Ln in sludge + $FeCl_2 \rightarrow LnCl_3$ + Fe–alloy

Ln_2O_3 in sludge + C + $FeCl_2 \rightarrow LnCl_3$ + CO

Possible to chlorinate only rare earth, regardless of metallic or oxide state without chlorination of iron.

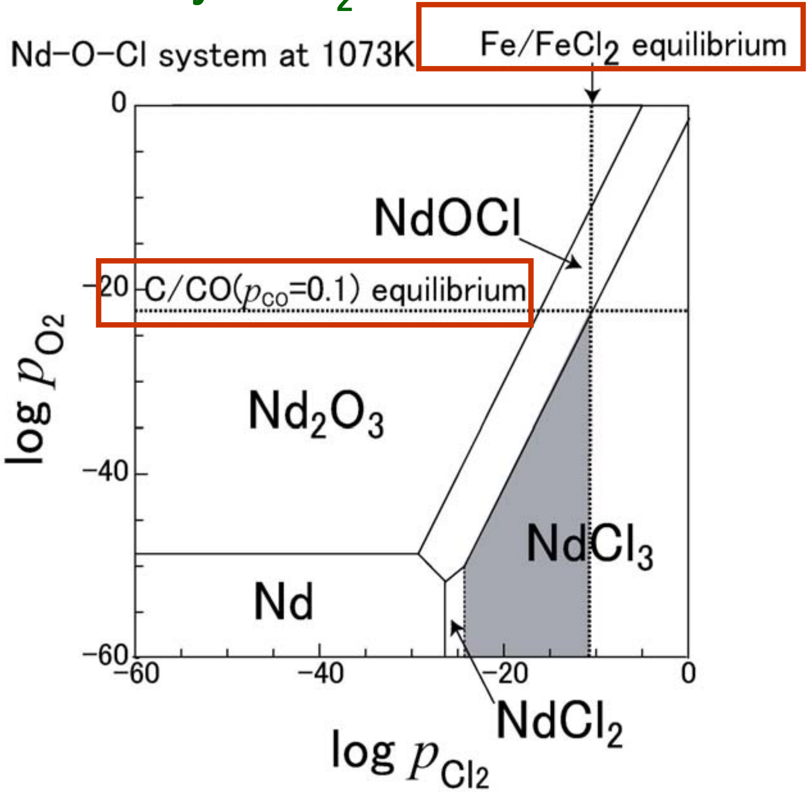
Thermodynamics

Propose recycling process of chlorination by $FeCl_2$

Ln in sludge + $FeCl_2$
$\rightarrow LnCl_3$ + Fe–alloy

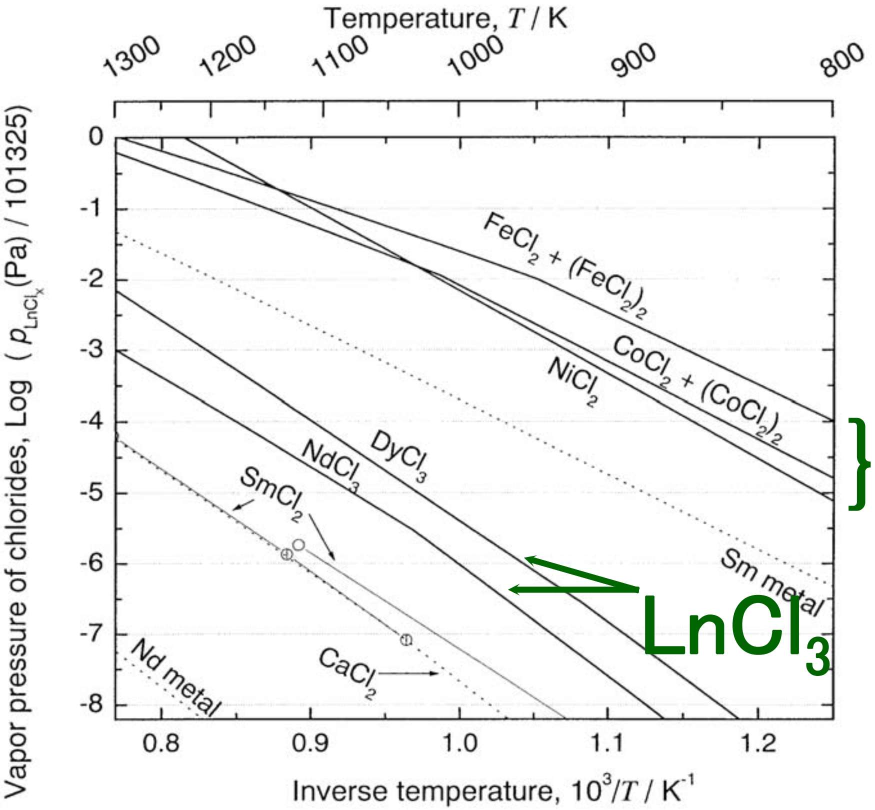
Ln_2O_3 in sludge + C + $FeCl_2$
$\rightarrow LnCl_3 + CO$

Ln : Lanthanoid



In the gray area, metallic iron can equilibrate with neodymium trichloride.

Vapor Pressure

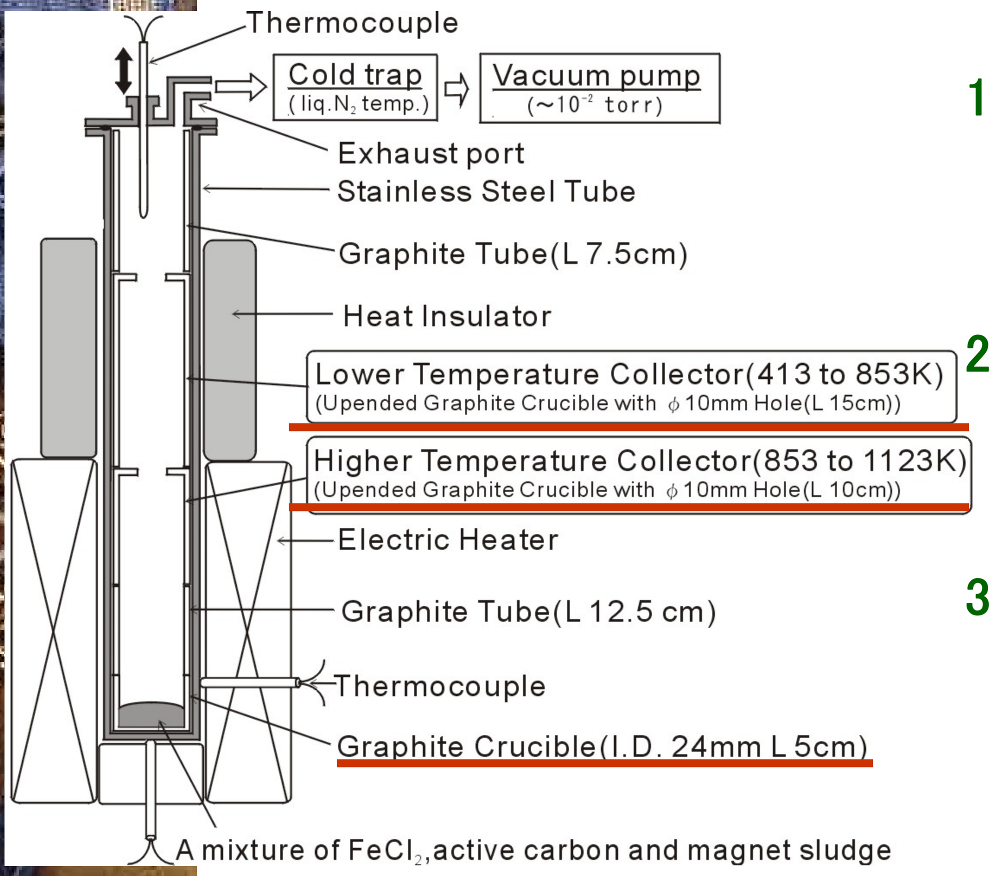


} $FeCl_2$, $CoCl_2$, $NiCl_2$

$LnCl_3$

- Vapor pressure of rare earth chloride are three orders of magnitude smaller than $FeCl_2$. Thus, it is expected to be easy separation by distillation.

Experimental



Composition of received sludge

(61.2%Fe−24.1%Nd−4.5%Dy−1.0%B)+Al,Co

1. $FeCl_2$(15g, excess amount)、activated carbon(1g) and sludge(5g) are mixed.
2. Heated to 1073K for 12h in Ar *(Extraction of Ln to molten $FeCl_2$ phase.)*
3. Vacuum Distillation at 1273K for 3h *(Separation between $LnCl_3$ and excess $FeCl_2$)*
4. Recovering deposit at lower and higher temperature collector

Experimental results

1) Selective extraction

Initial 61.2%Fe–24.1%Nd–4.5%Dy–1.0%B)+Al,Co

(a)	Composition of Fe, Nd, Dy and B				Other Elements detected by XRF
	c_i / mass %				
	Fe	Nd	Dy	B	
Initial Sludge	61.16	24.12	4.47	1.00	Al, Co
		↓	↓		
After Exp.	79.43	0.66	0.18	0.57	Co, Cl
(b) Extraction ratio(%)		Nd	Dy		Ave.
		96.2	94.2		95.9

- Extraction ratio was larger than 95 %.

The extraction by chlorination using iron chloride is very easy.

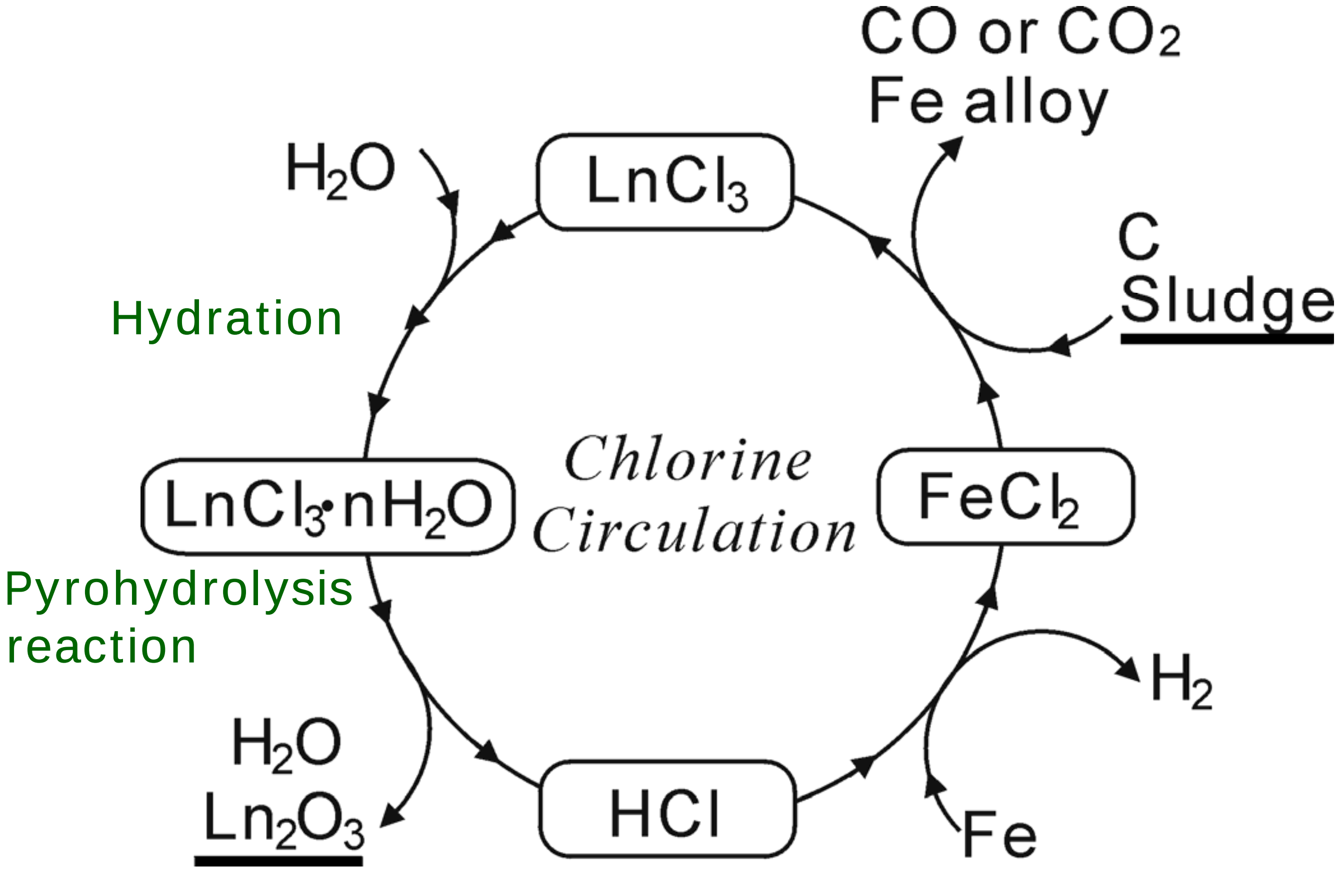
Experimental results

2) Distillation

	Cationic mass % of Fe, Nd, Dy、B				
	c_i / $(c_{Fe} + c_{Nd} + c_{Dy} + c_B) \times 100$				
	Fe	Nd	Dy	B	(Nd + Dy)
Higher Temp. Collector	0.8	82.4	16.8	n.a.	99.2
Lower Temp. Collector	98.7	0.7	0.3	0.2	1.0

- It is possible to recover high purity rare earth chloride by distillation.

Propose new recycling process



- In this process, only carbon & water are consumed.
- By-product are only iron alloy, CO, CO_2 and H_2

Further Possibility

This proposed process is not limited to Nd magnet.

Thermodynamic view point : $FeCl_2$ does not chlorinate Co and Ni

- Sintered Magnet
  - Nd-Fe-B (This study)
  - Sm-Co
- Bonded Magnet(formed by epoxy resin instead of sintering process)
  - Nd-Fe-B, Sm-Co, Sm-Fe-N

Epoxy is expected as carbon source.

- La-Ni (Mm-Ni) Hydrogen storage alloys

↓

- This process can be applied to any alloys consisted of rare earth and the element of iron group.
- Any waste contaminated by oxygen, nitrogen, machine oil & plastic are welcome.

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Anodic Dissolution Behavior of Titanium in Room Temperature Molten Salt (TMHA-Tf_2N)

Hidekazu Nakagawa, Tetsuya Uda,
Kuniaki Murase, Yasuhiro Awakura
Kyoto University

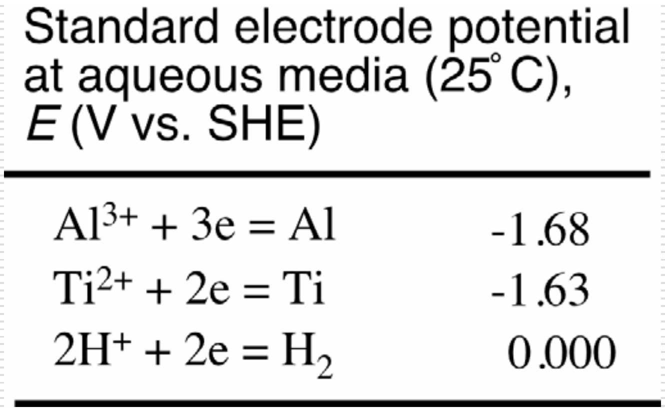
Introduction

Titanium has an excellent corrosion resistance.

However, the application of bulk titanium is limited because it costs so much to refine from ore.

Electroplating a titanium layer

It is difficult to electrodeposit titanium from aqueous media



Standard electrode potential at aqueous media (25°C), *E* (V vs. SHE)

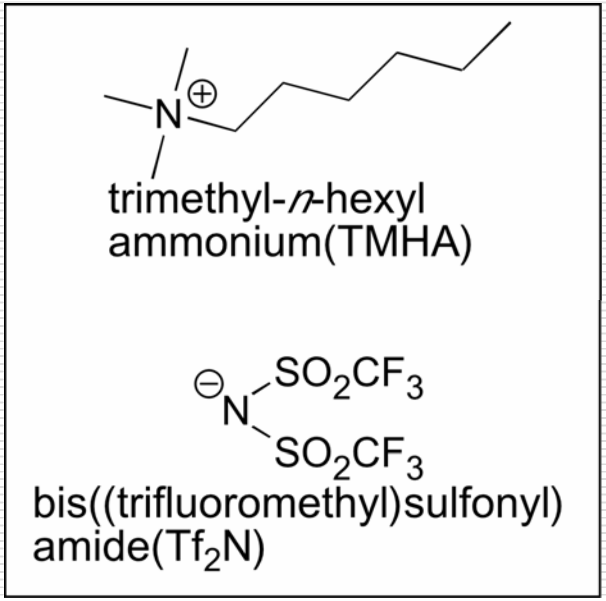
$Al^{3+} + 3e = Al$	-1.68
$Ti^{2+} + 2e = Ti$	-1.63
$2H^{+} + 2e = H_2$	0.000

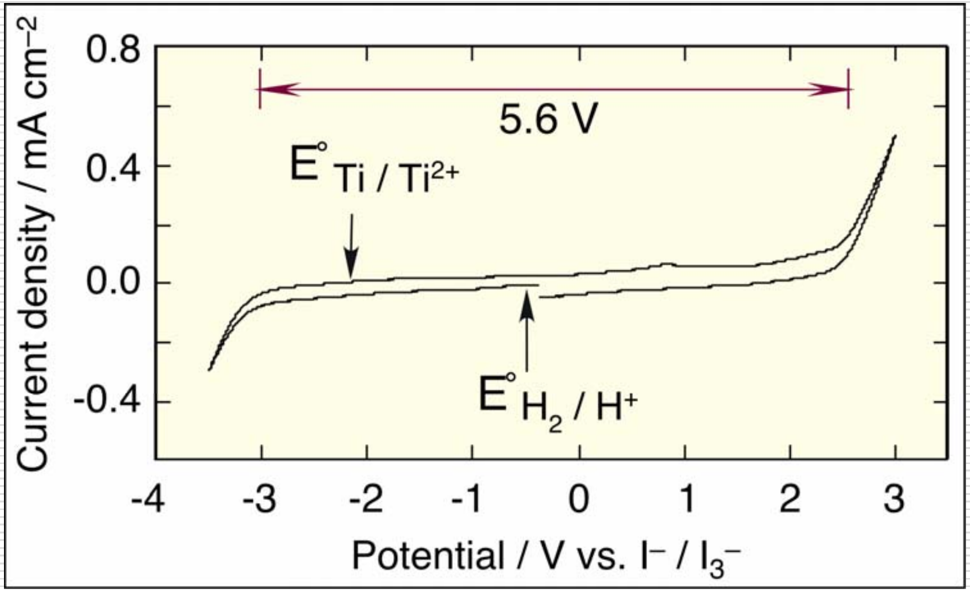
Room Temperature Molten Salts (ionic liquids) have been developed.

- New electrolyte for electrodeposition of reactive metals

Room Temperature Molten Salt, “TMHA-Tf$_2$N”

Ammonium-Imide type room temperature molten salt





Cyclic voltammogram for TMHA-Tf$_2$N

WE, CE : Pt Temperature : 50 °C

- Wide electrochemical window
- Ease of synthesis

As a first step for electroplating of titanium, we investigated the anodic dissolution of a titanium electrode.

Why anodic dissolution?

Reason 1.

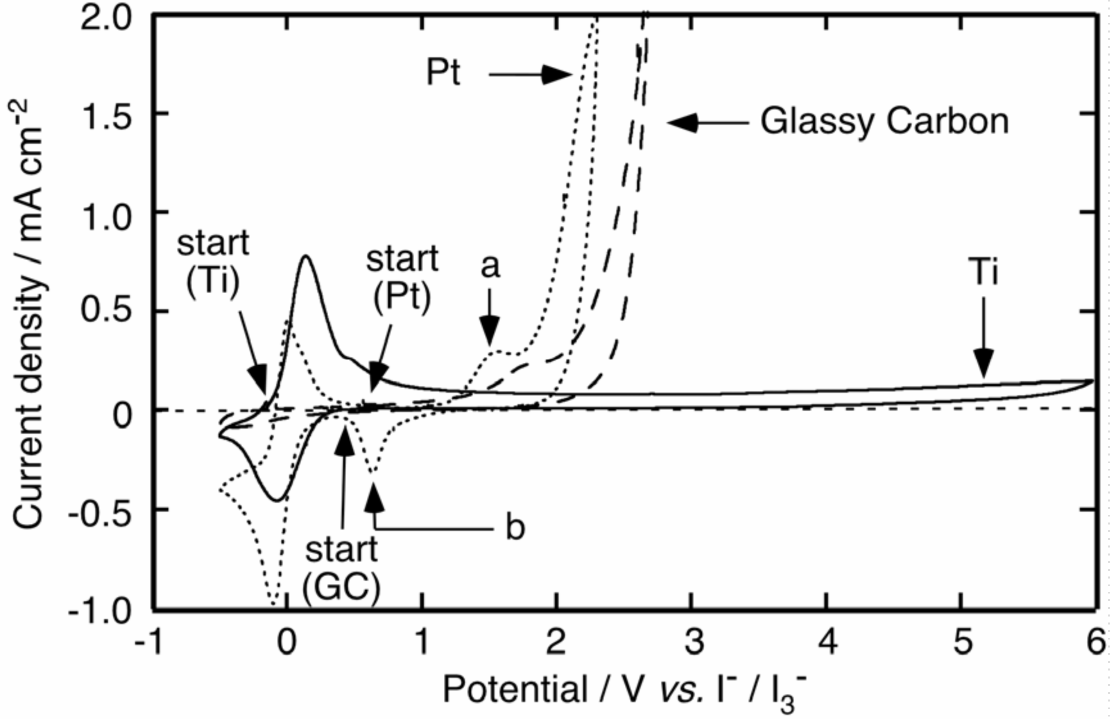
To feed titanium ions into TMHA-Tf_2N by anodic dissolution of a titanium electrode, if possible, it is quite easy method.

Reason 2.

As the kinetics of electrochemical dissolution of metals are sometime similar to that of electrochemical deposition,

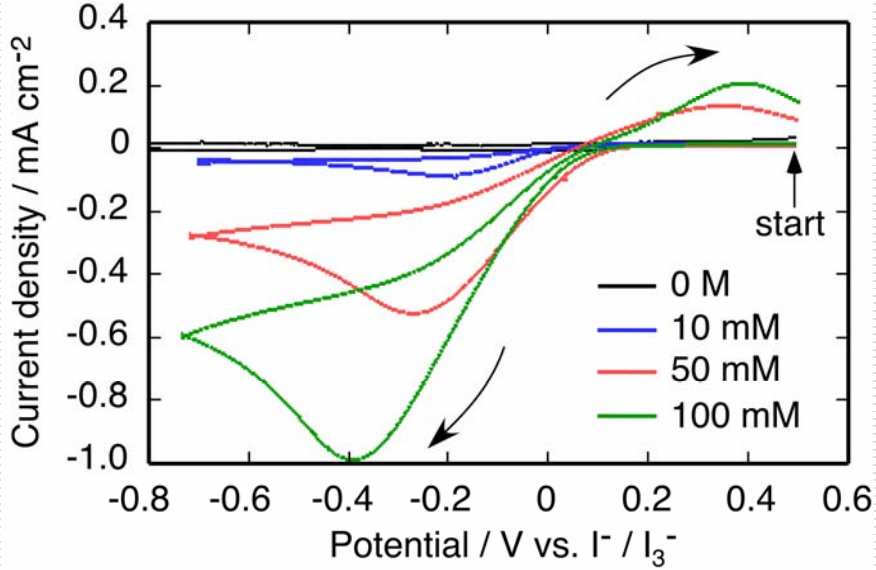
it is worth to investigate the anodic dissolution behavior for electrodeposition of titanium.

Comparison of cyclic voltammograms on Pt, Glassy Carbon and Ti electrode.

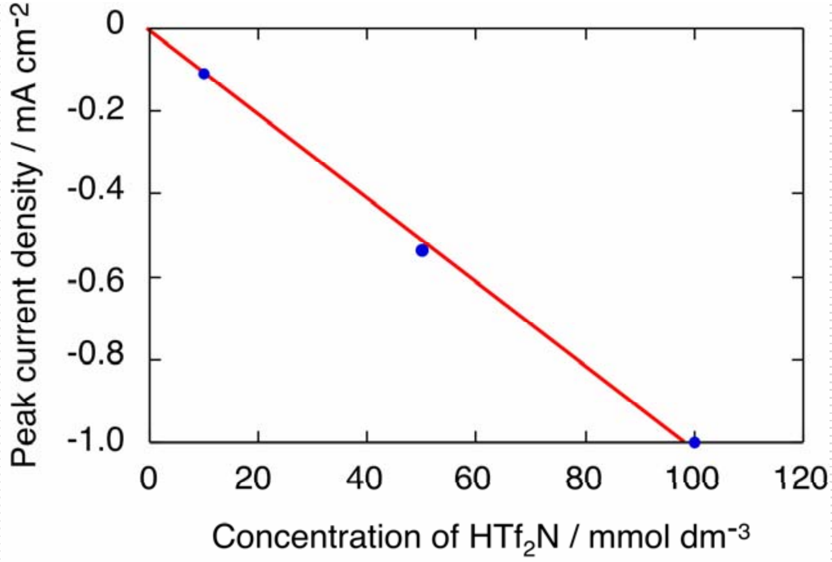


- •Anodic current of decomposition of molten salts stood up at around 2V on Pt,glassy carbon electrode.
- •The peak “a” and “b” on platinum electrode corresponds to anodic dissolution and cathodic deposition of Pt.
- •There is redox couple at around -0.15 V on Pt, Ti electrode

Reaction at -0.15 V



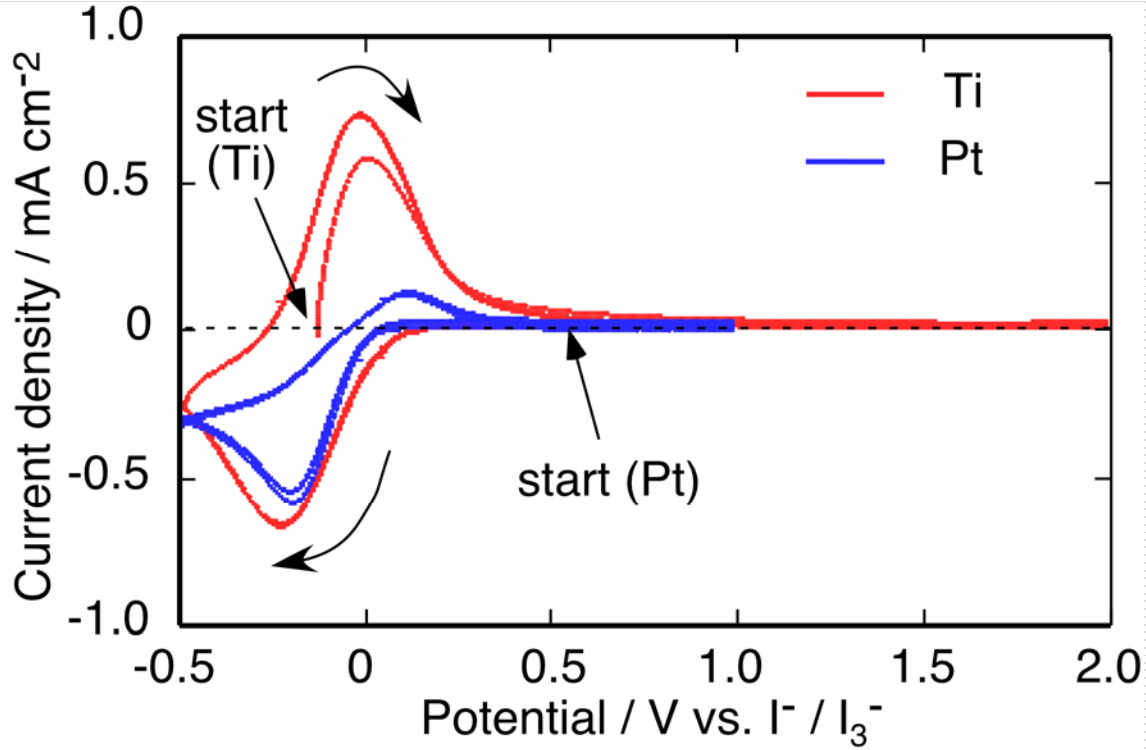
Concentration of proton was changed from 0 mM to 100 mM



The relationship between peak cathode current and concentration of proton

The redox reaction at -0.15 V is the reduction of protons and oxidation of hydrogen.

Cyclic voltammogram on platinum electrode



Bath : 50 mM HTf_2N – TMHA-Tf_2N solution

WE : Ti, Pt

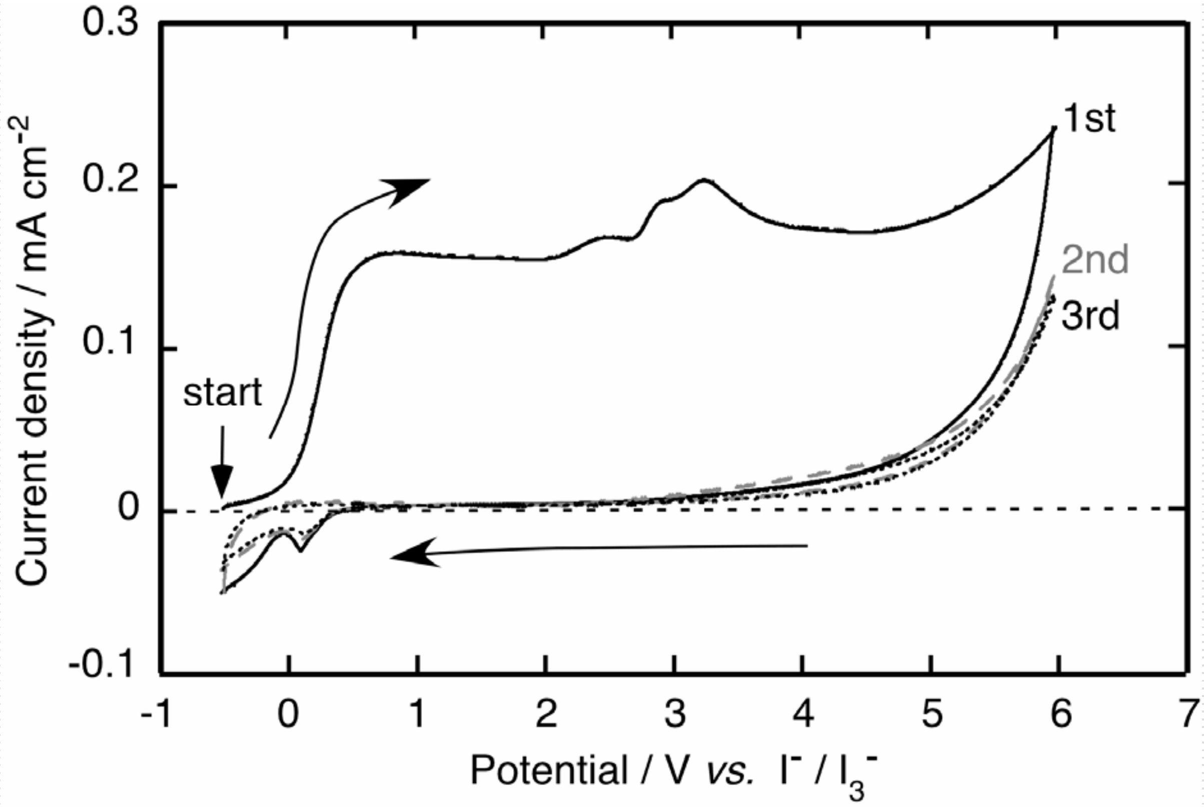
CE : Ti

Temperature : 50 °C

Scan rate : 10 mV s^{-1}

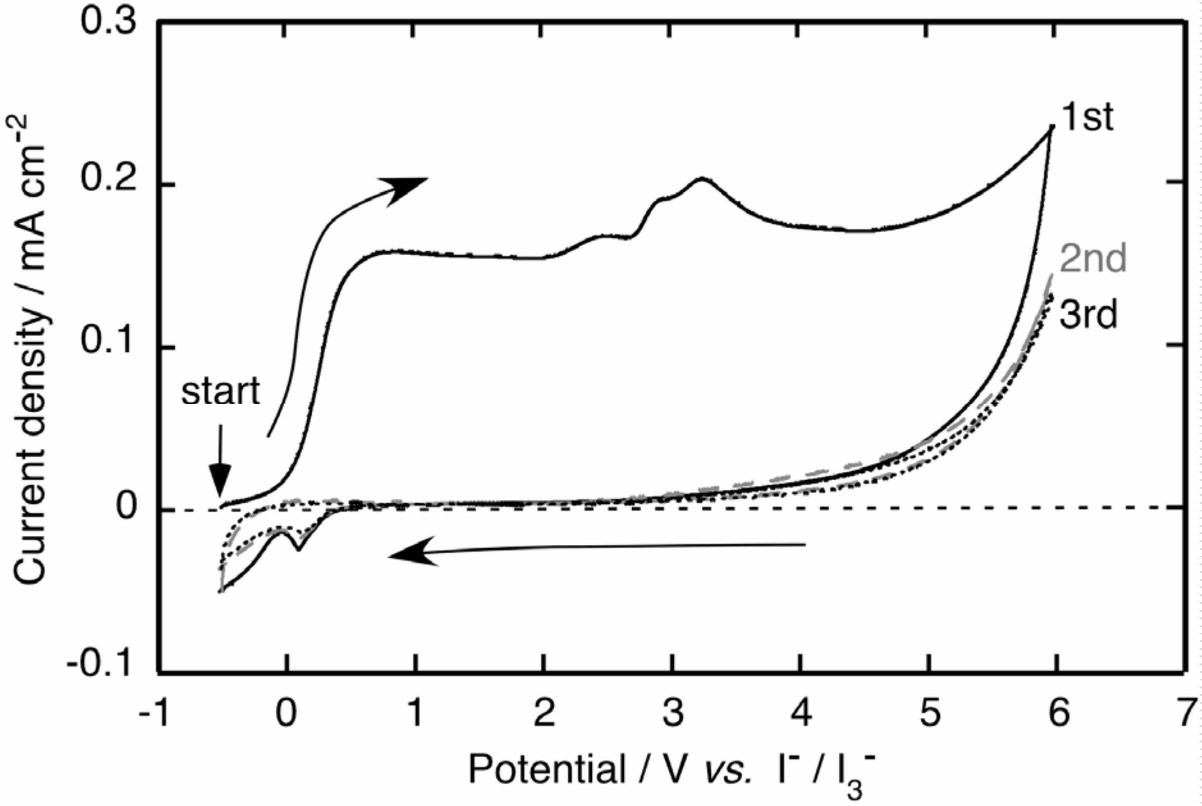
Titanium does not anodically dissolve?

Mechanically polished in Glove Box



The titanium electrode was used just after mecallycally polished in glove box.

Mechanically polished in Glove Box



- •A large hysteresys
- •No reaction on 2nd and 3rd cycles

A bit strange?

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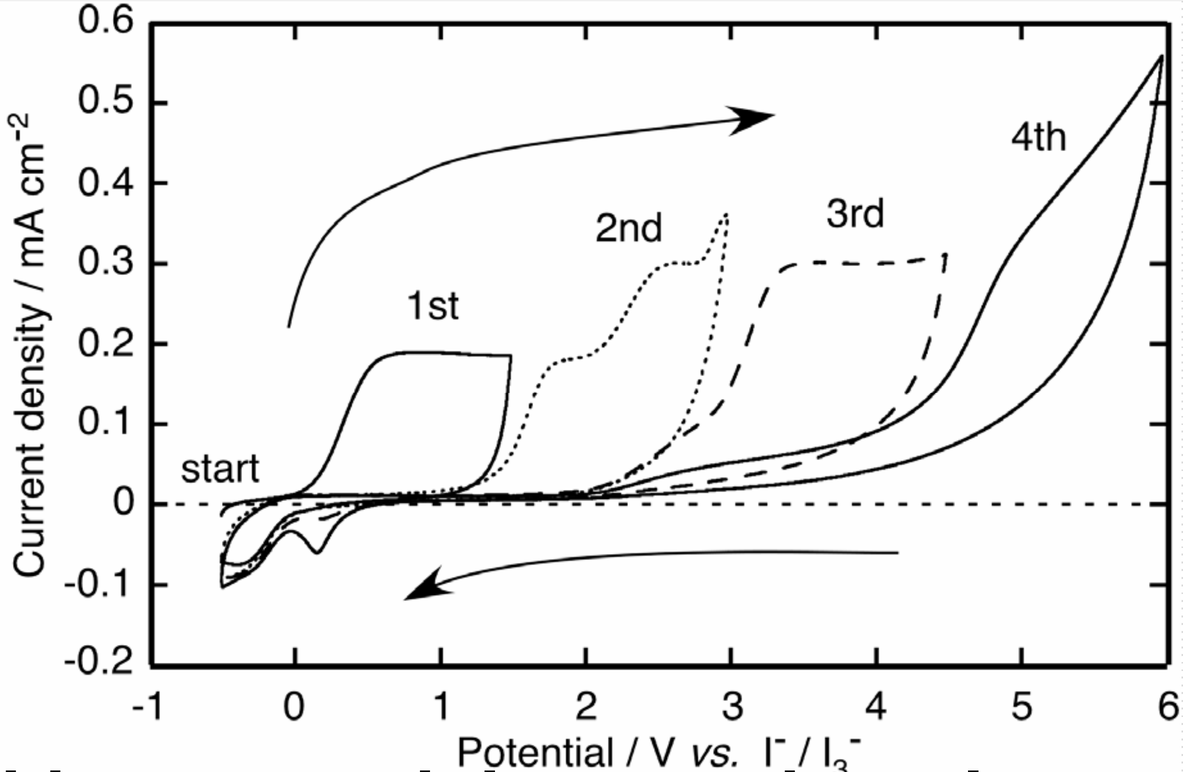
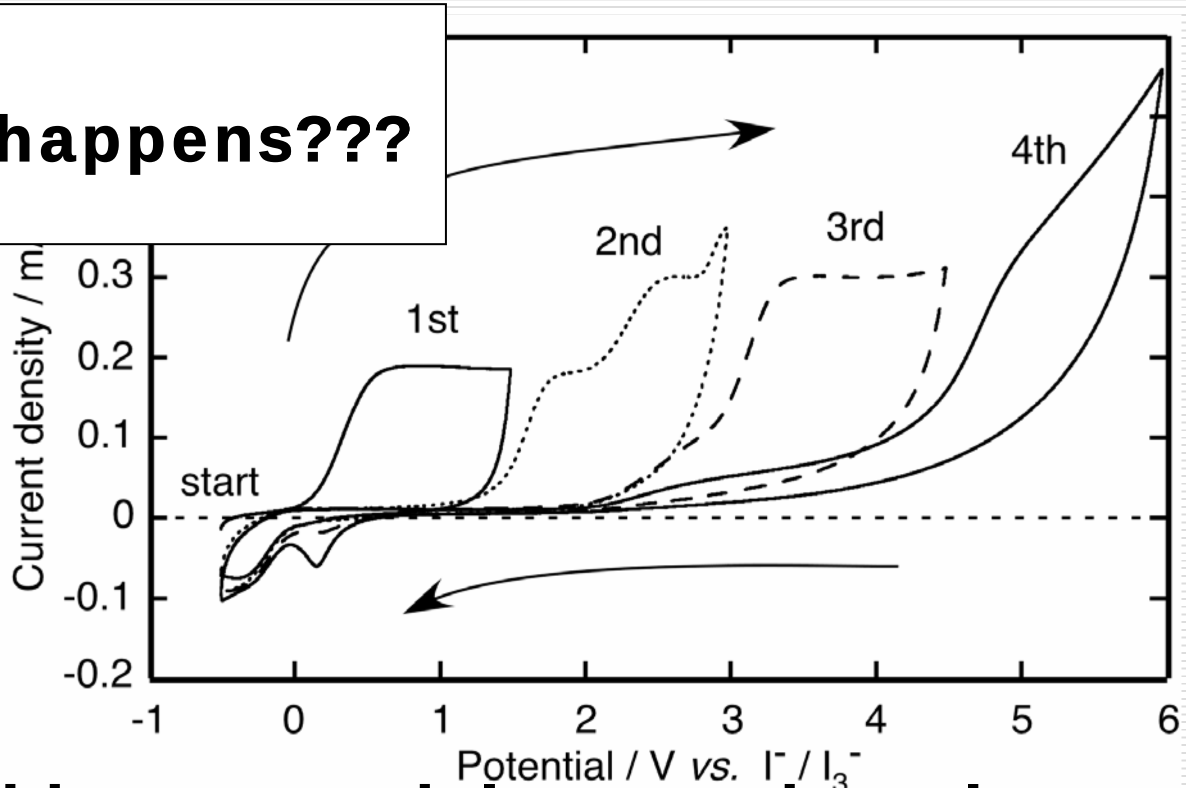


- •Switching potentials at each cycle were changed.
- •Anodic current stood up at the previous switching potential.
- •It looks like titanium electrode memorized the previous switching potential.

Mechanically polished in Glove Box

What happens???



- **Switching potentials at each cycle were changed.**
- **Anodic current stood up at the previous switching potential.**
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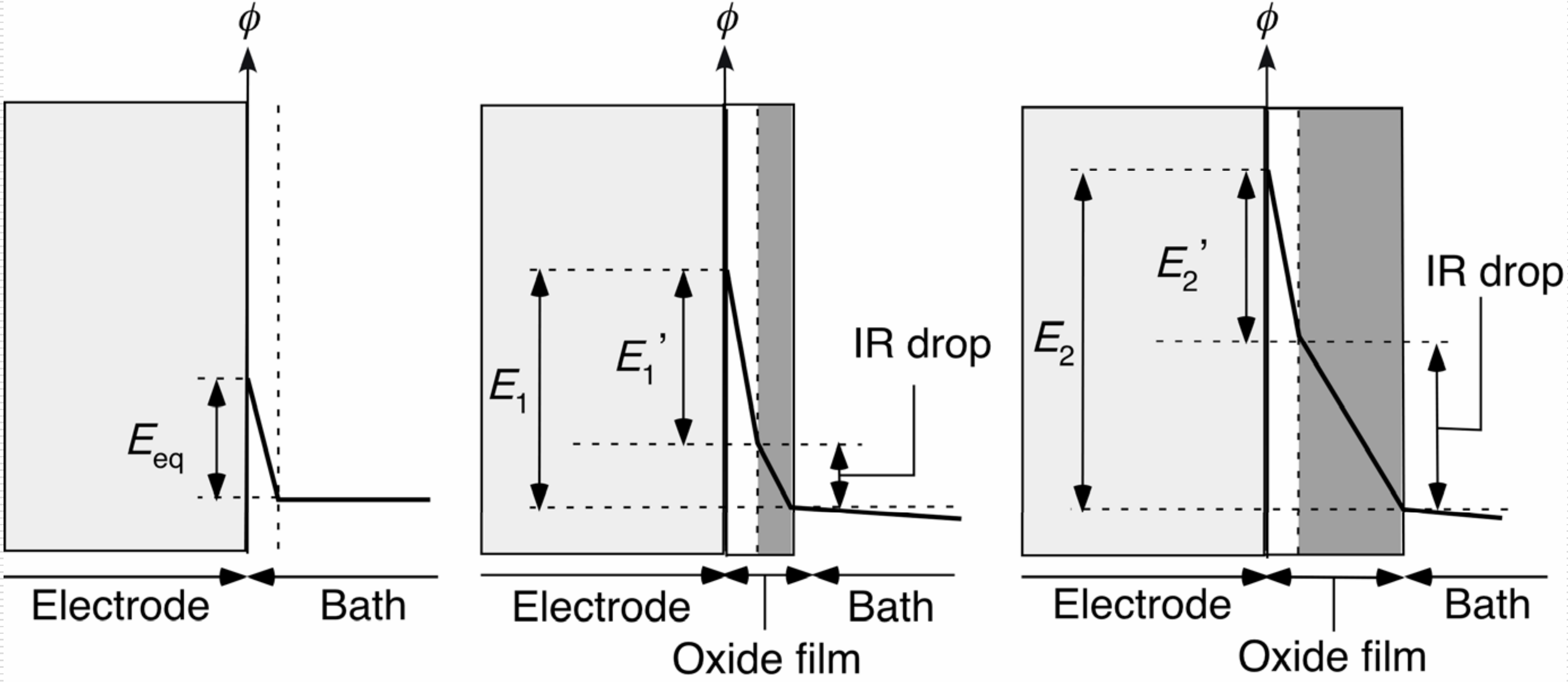

To explain such complex behavior,
We assumed a formation of thin titanium oxide film on titanium electrode during the positive polarization.

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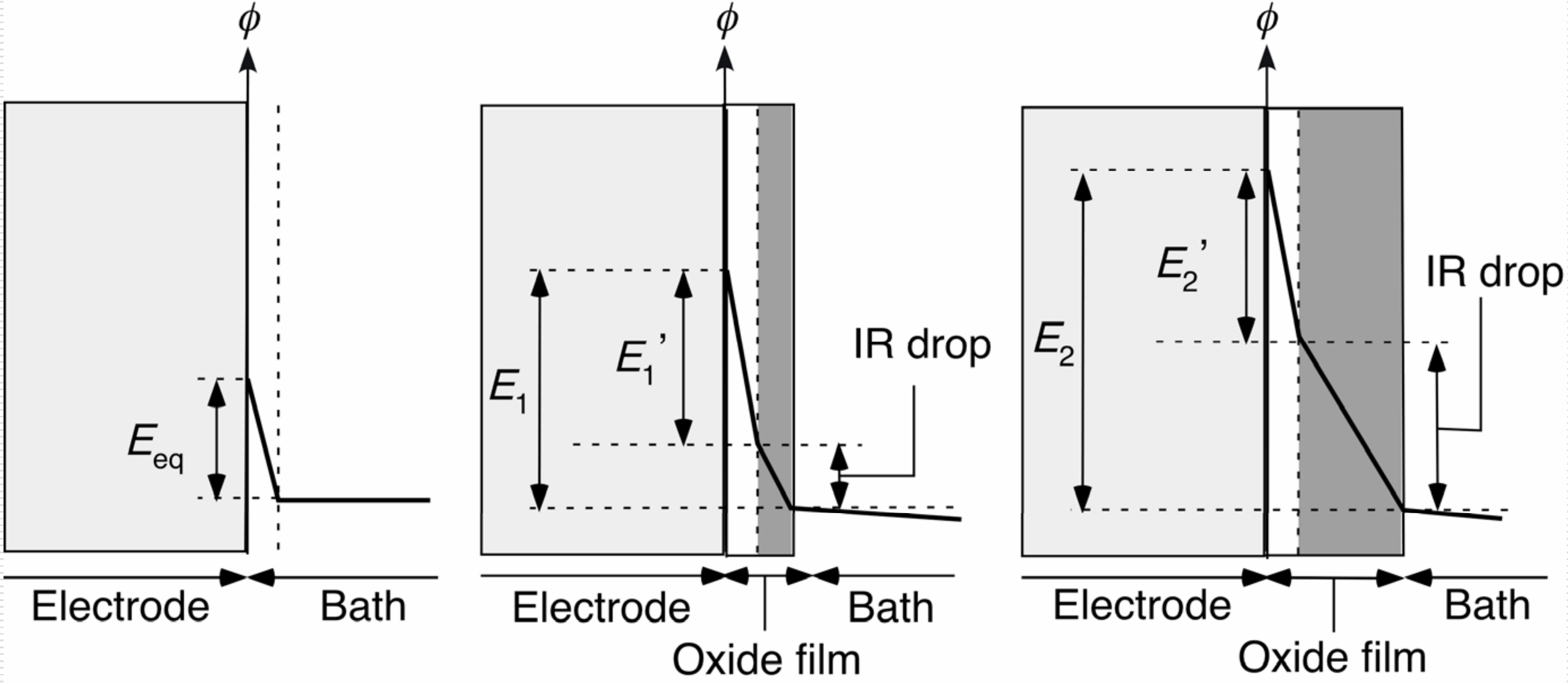
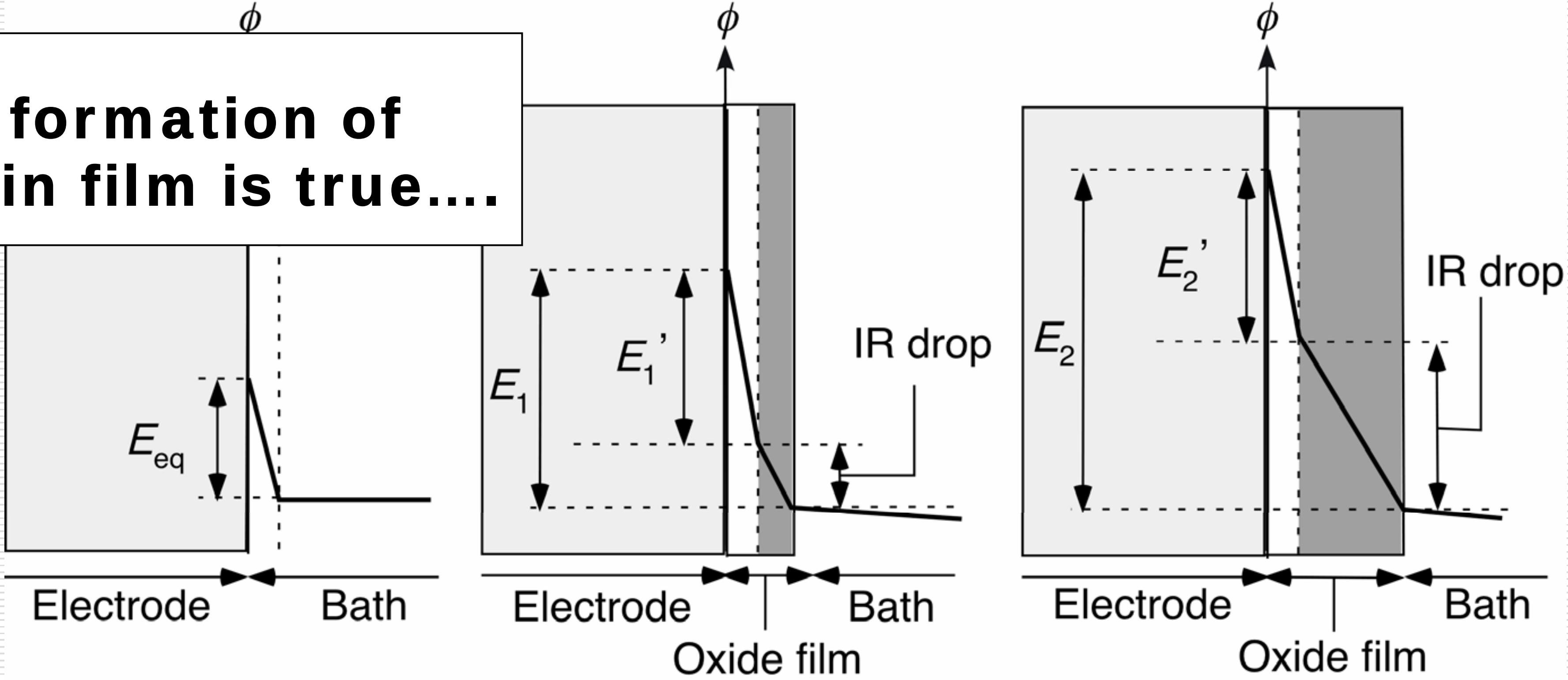


The assumed reaction of formation of titanium oxide film is

$2x\,H_2O$ in molten salt + Ti → $4x\,H^+ + TiO_x + 4x\,e^-$

Mechanically polished in Glove Box

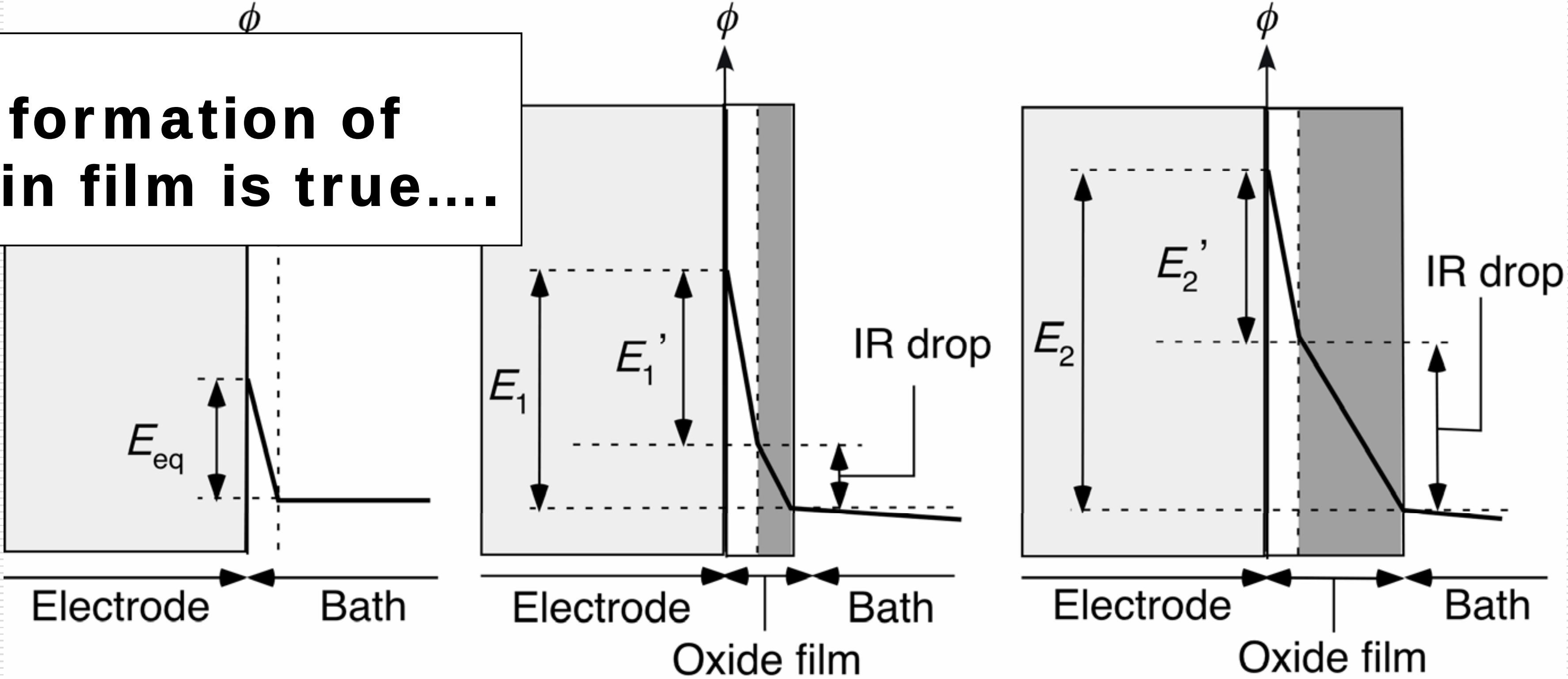
If formation of thin film is true….



1. A large part of voltage is consumed as IR drop because of the large resistivity of the oxide film.
2. Then the real electrode potential on the electrode is much smaller than the monitored potential.
3. The thickness of the titanium oxide film increased with the amount of electric charge passed through the electrode,but the current will stop without sweeping potential to positive direction.

Mechanically polished in Glove Box

If formation of thin film is true....



4. The thin titanium oxide film remains on the titanium surface after the anodic polarization.
5. It means that the electrode memorizes the previous switching potential.
6. As the result of high resistivity of the thin titanium oxide film, it is difficult to apply enough potential to start anodic decomposition of molten salt.

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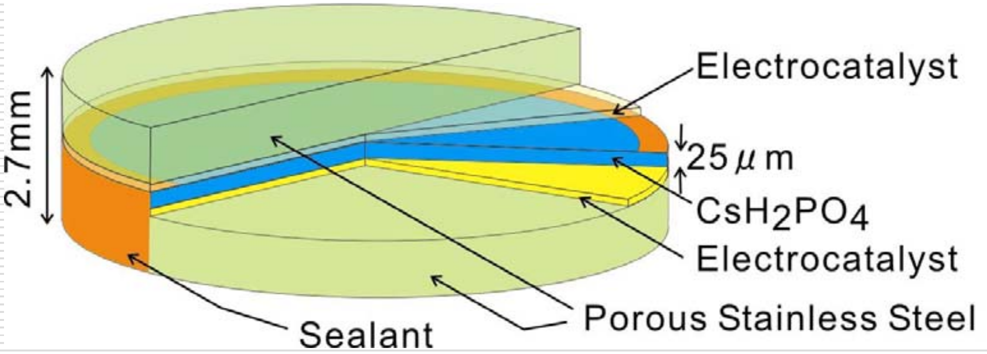
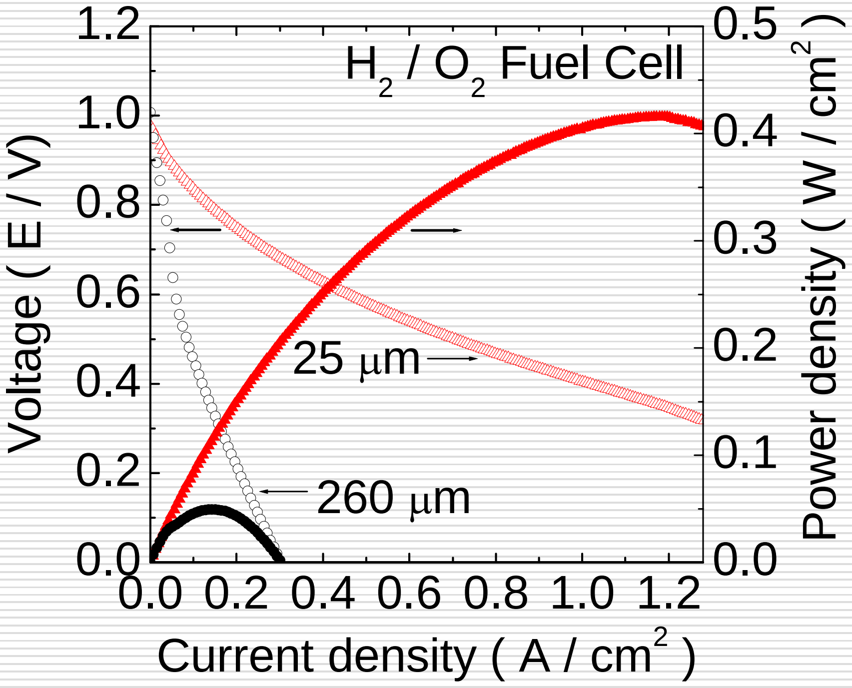
Joint Research with Superprotonic, Inc.,CA, USA





The performance is almost double than phosphoric acid fuel cell.

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Kyoto

Only two and half hours from Tokyo by train.Please visit our lab anytime.

tetsuya-uda@mtl.kyoto-u.ac.jp

Thanks for your attention!