Cathodic Polarization Behavior of Ionic Liquid Containing Titanium Ions

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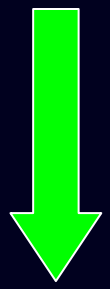
Introduction

Ti

- Titanium has an excellent corrosion resistance.
- The application field of bulk titanium is limited because of high costs to refine from the ore.

Electroplating of a titanium layer



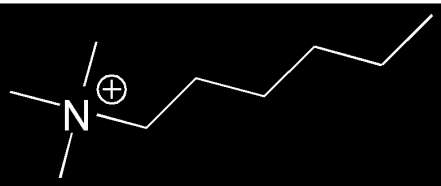
Electroplating of titanium in aqueous media is almost impossible.

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

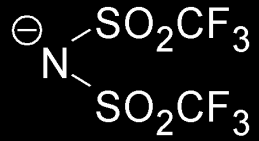
$Ti^{2+} + 2e = Ti$	-1.63
$Al^{3+} + 3e = Al$	-1.68
$2H^{+} + 2e = H_2$	0.00

In Ionic Liquid (room temperature molten salt)

Ionic Liquid (TMHA-Tf_2N)

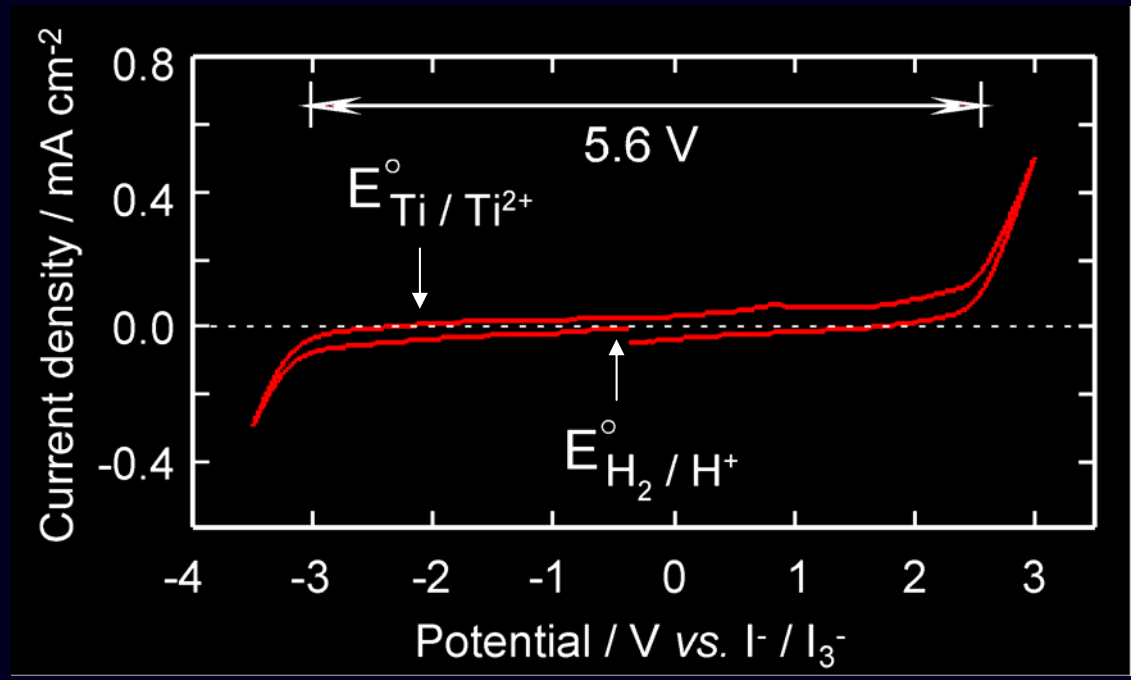


trimethyl-*n*-hexyl ammonium(TMHA)



bis((trifluoromethyl)sulfonyl) amide(Tf_2N)

TMHA-Tf_2N



Wide electrochemical window

Strategy

Electrodeposition of titanium in ionic liquid (Final target)

To feed titanium ions into ionic liquid by

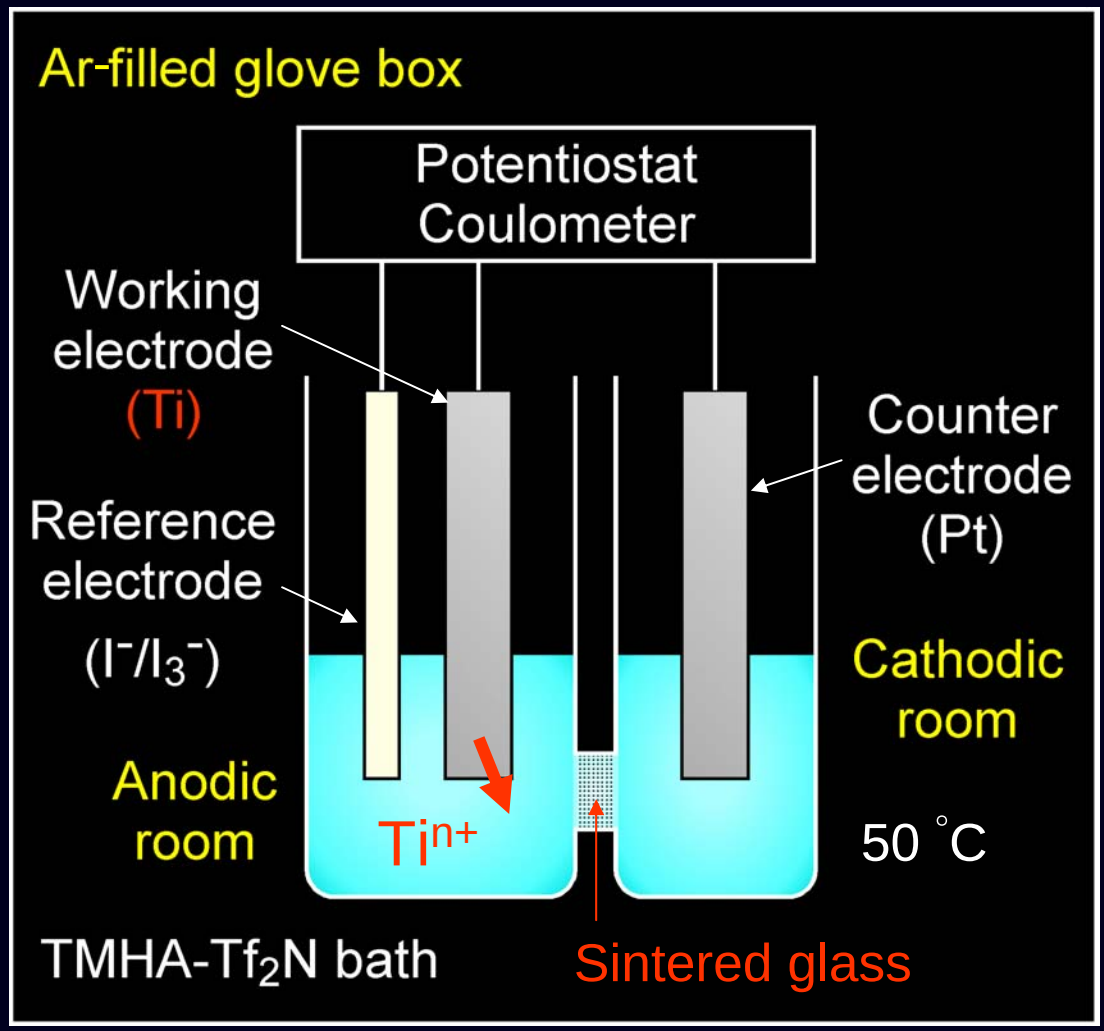
- Anodic dissolution of titanium electrode

After anodic dissolution of titanium, we investigate the cathodic polarization behavior of the solution containing titanium ions.

Contents

- Anodic dissolution of titanium
- Cathodic polarization behavior of ionic liquid containing titanium ions

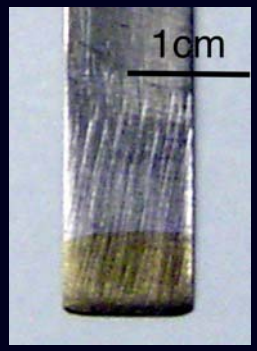
Apparatus (anodic dissolution of titanium)



Anodic polarization of titanium

E (*vs*. I^- / I_3^-)	slow polarization (cyclic voltammogram)	quick polarization (potentiostatic electrolysis)
< around 7 V	×	×
around 7 V <	×	○

×

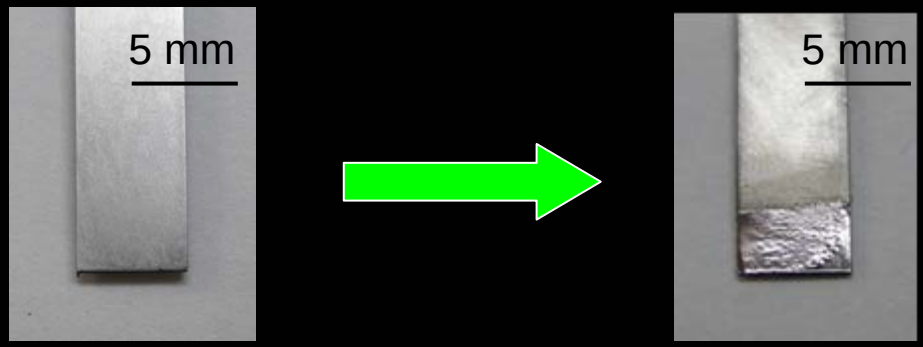


Titanium oxide film formed.

Anodic dissolution of titanium

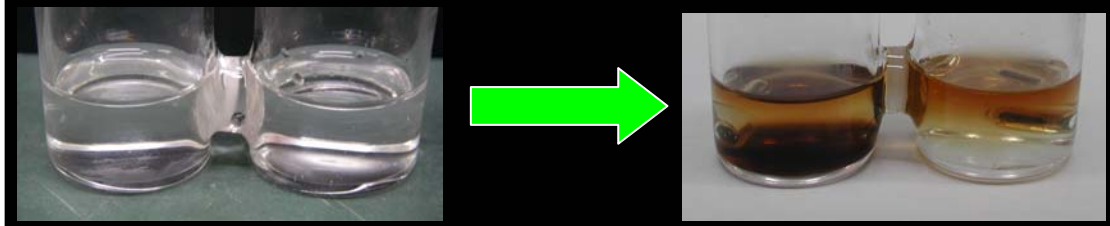
- Potentiostatic electrolysis at 9 V *vs.* I^- / I_3^-

Titanium electrode



Titanium dissolved !!

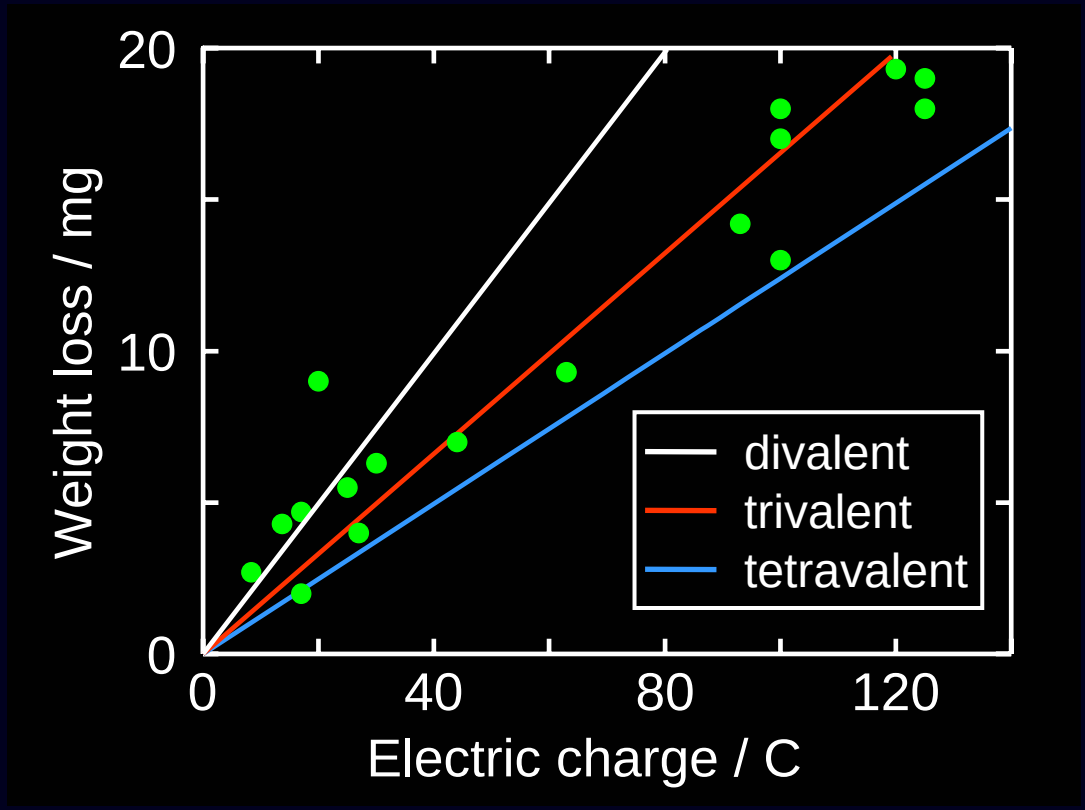
Ionic liquid



Ionic liquid decomposed

at the same time !!

Weight loss of titanium electrode after the anodic electrolysis

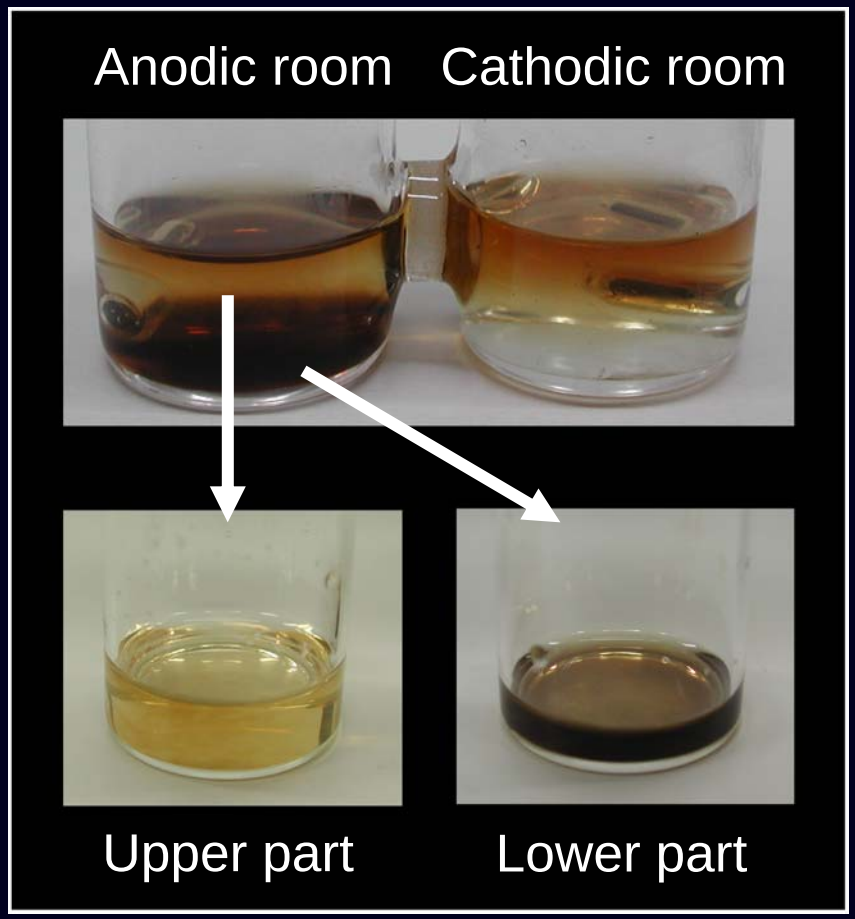


Current efficiency

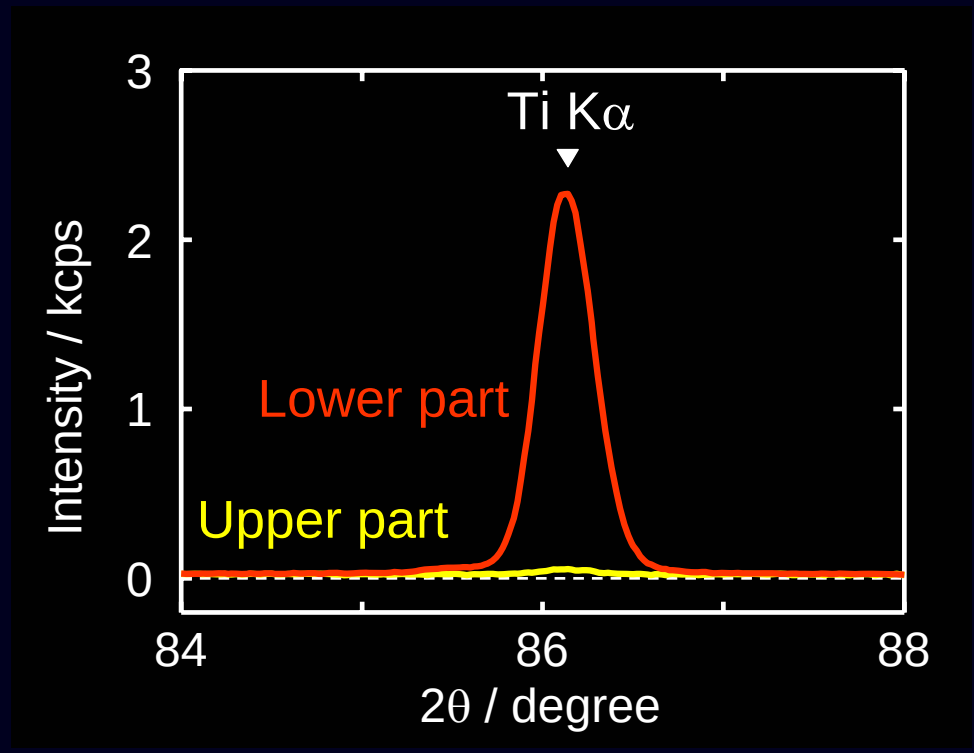
$Ti \rightarrow Ti^{2+} + 2e$	64 %
$Ti \rightarrow Ti^{3+} + 3e$	95 %
~~$Ti \rightarrow Ti^{4+} + 4e$~~	127 %

The titanium ions in ionic liquid would be divalent or trivalent.

Separation of ionic liquid in anodic room after the anodic dissolution



X-ray fluorescence (XRF) analysis



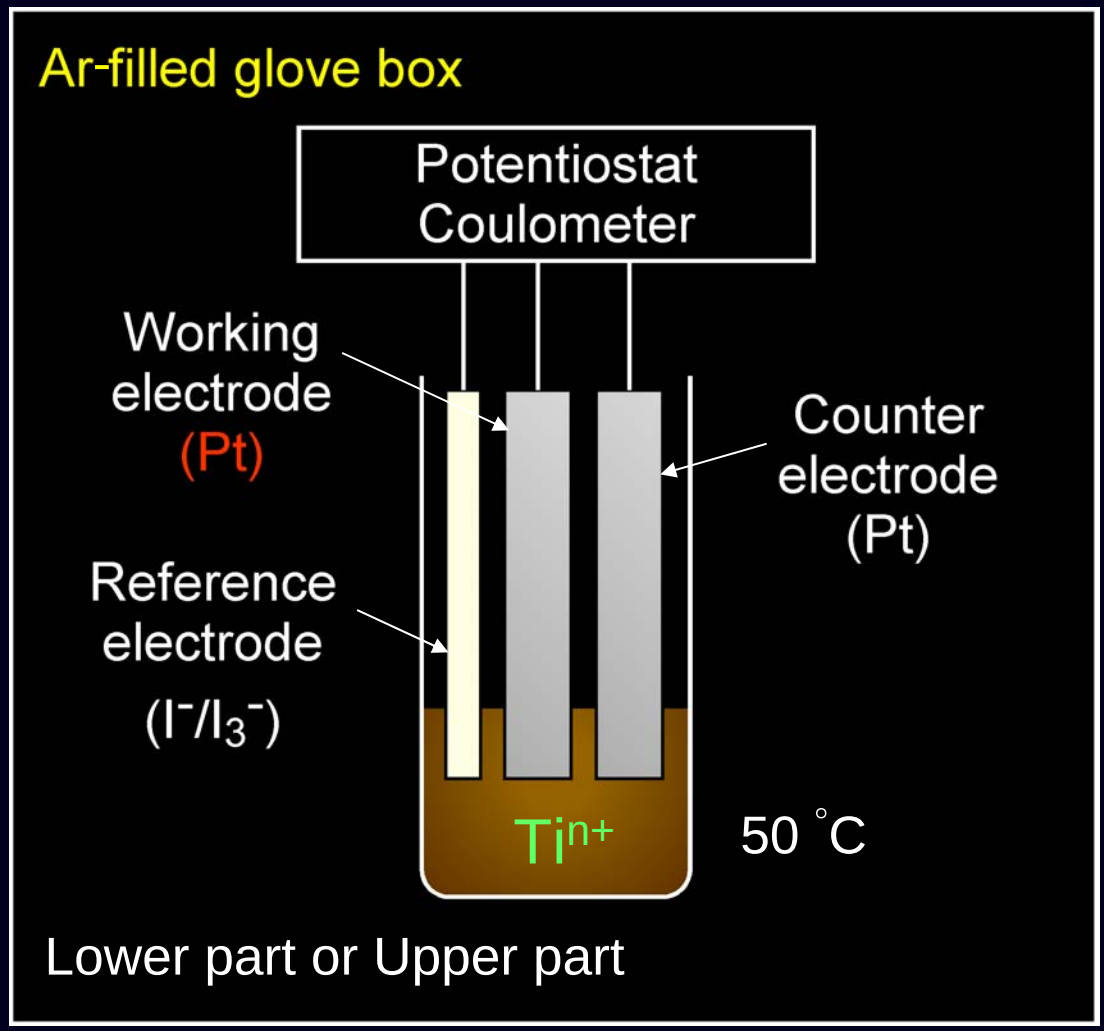
Separation into two parts

Titanium ions are contained in lower part.

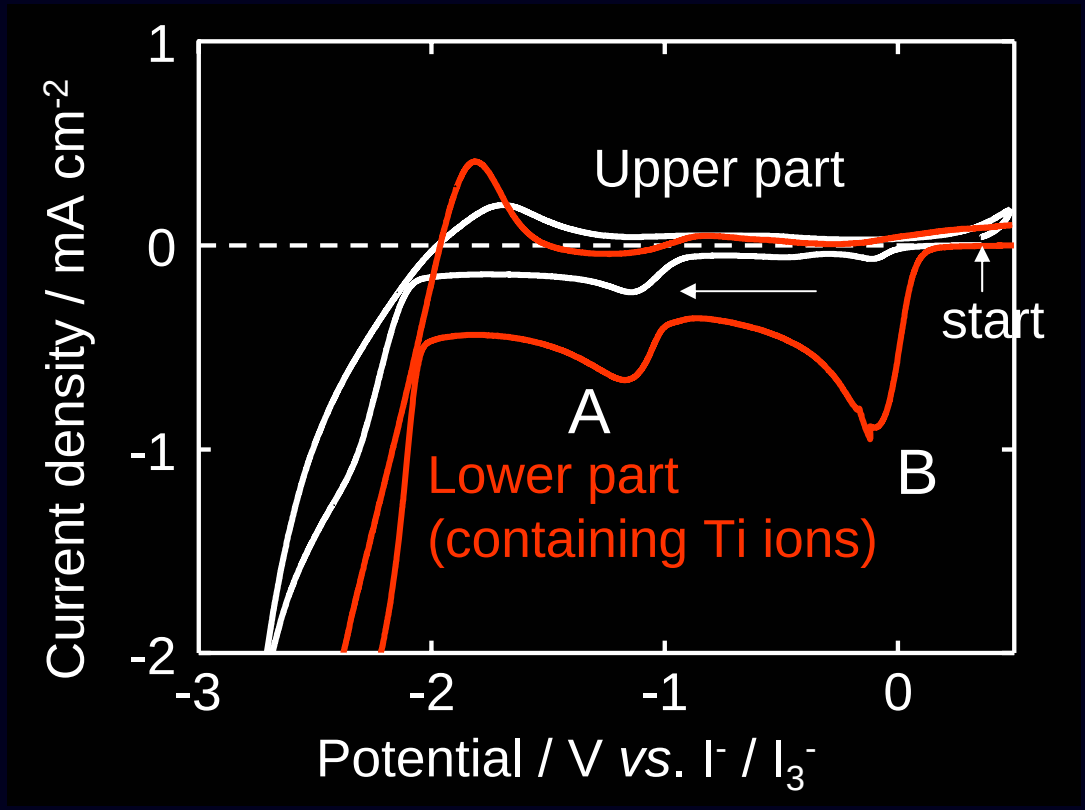
Contents

- Anodic dissolution of titanium
- Cathodic polarization behavior of ionic liquid containing titanium ions

Apparatus (cathodic polarization)



Cyclic voltammograms in upper and lower parts



Upper part

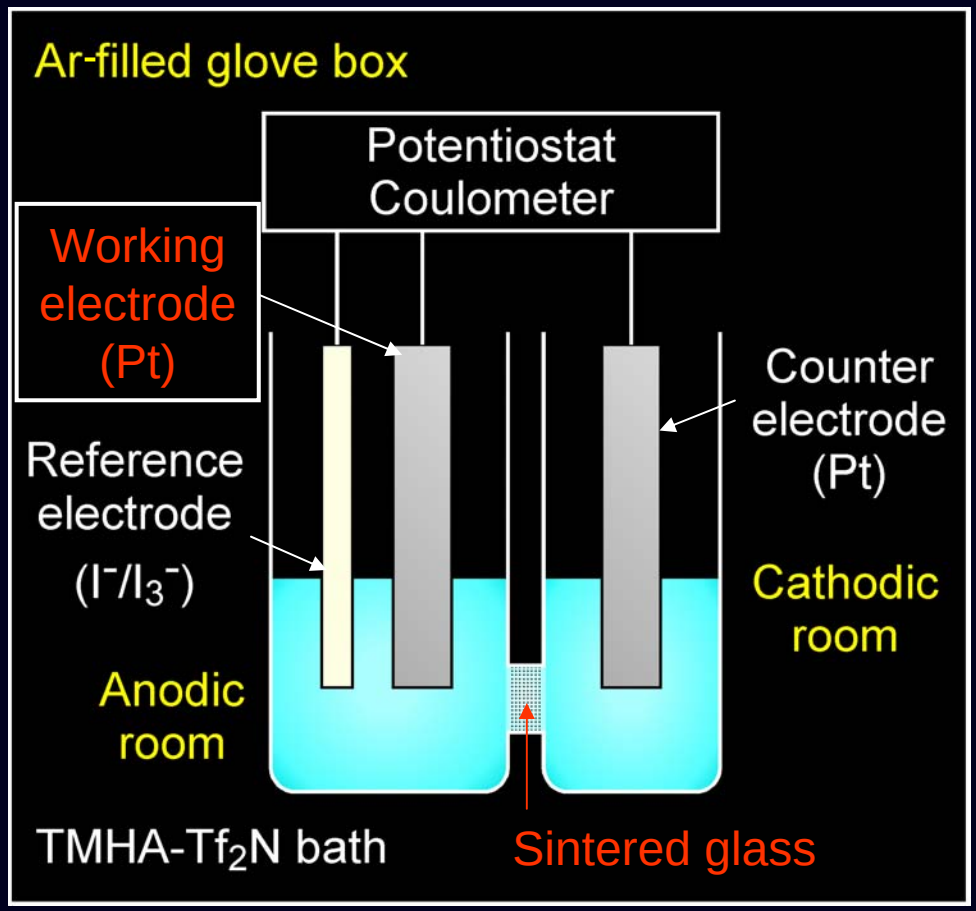
Lower part
(containing Ti ions)

WE, CE	:	Pt
Temperature	:	50 ˚C
Scan rate	:	10 mV/s

The peak B was observed in lower part containing titanium ions.

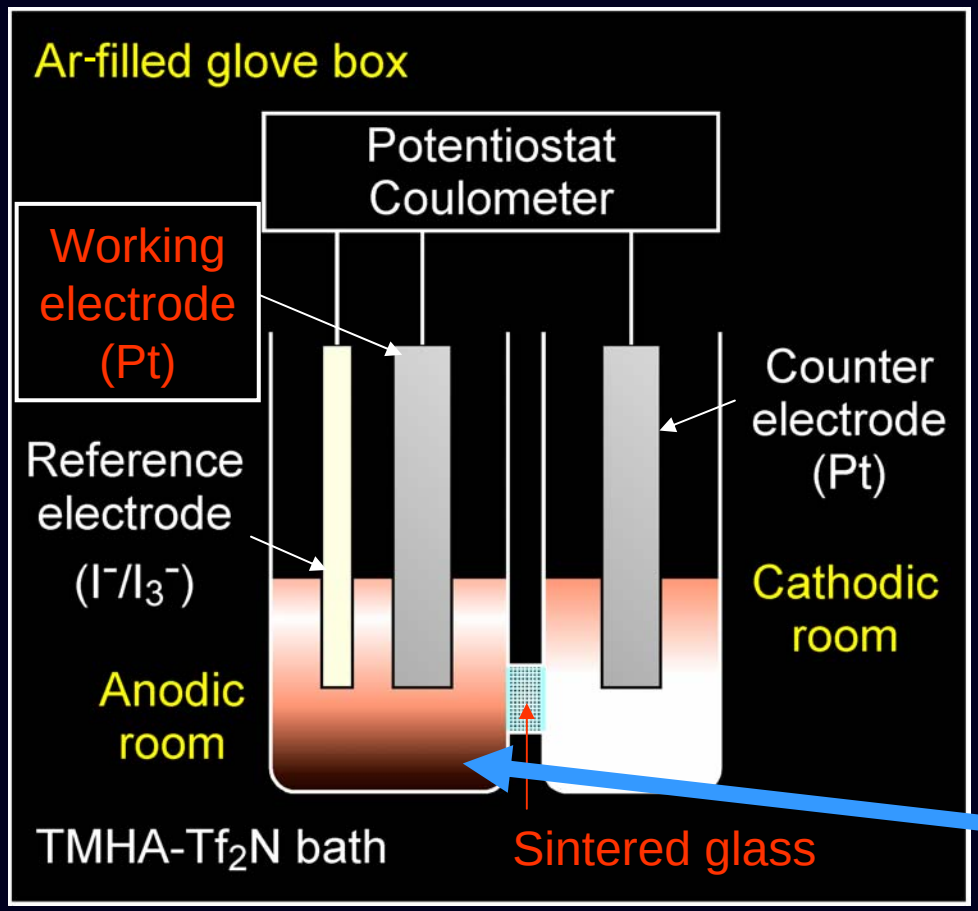
① The reduction of titanium ions ??
② The reduction of decomposition products ??

Influence of decomposition products



Decomposition of ionic liquid
(potentiostatic electrolysis at 9 V)

Influence of decomposition products

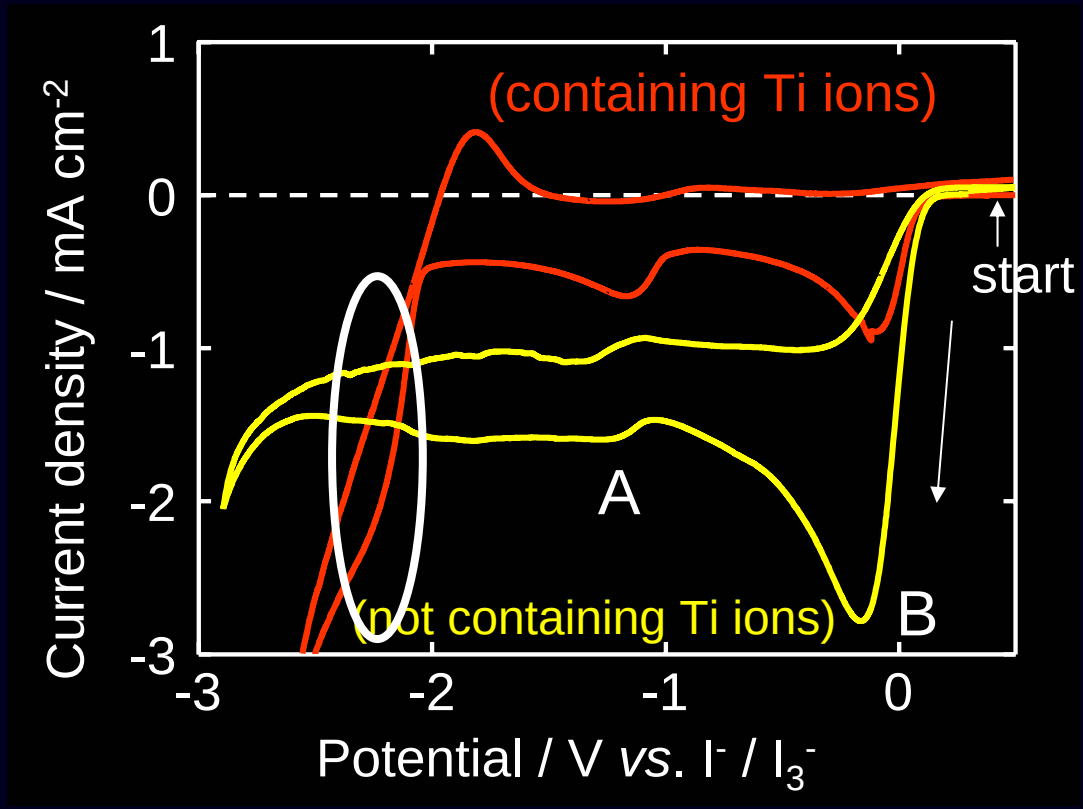


Decomposition of ionic liquid (potentiostatic electrolysis at 9 V)

Ionic Liquid of anodic room separated into two parts.

We took out lower part and carried out cyclic voltammetry.

Influence of decomposition products



WE, CE	:	Pt
Temperature	:	50 ˚C
Scan rate	:	10 mV/s

Despite not containing Ti ions, the peak B was observed.

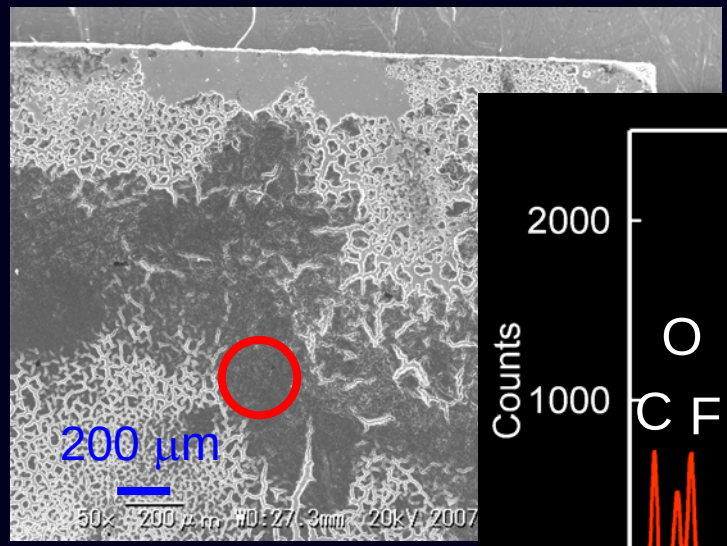
➡ ② Reduction of decomposition products.

Electrodeposition experiment

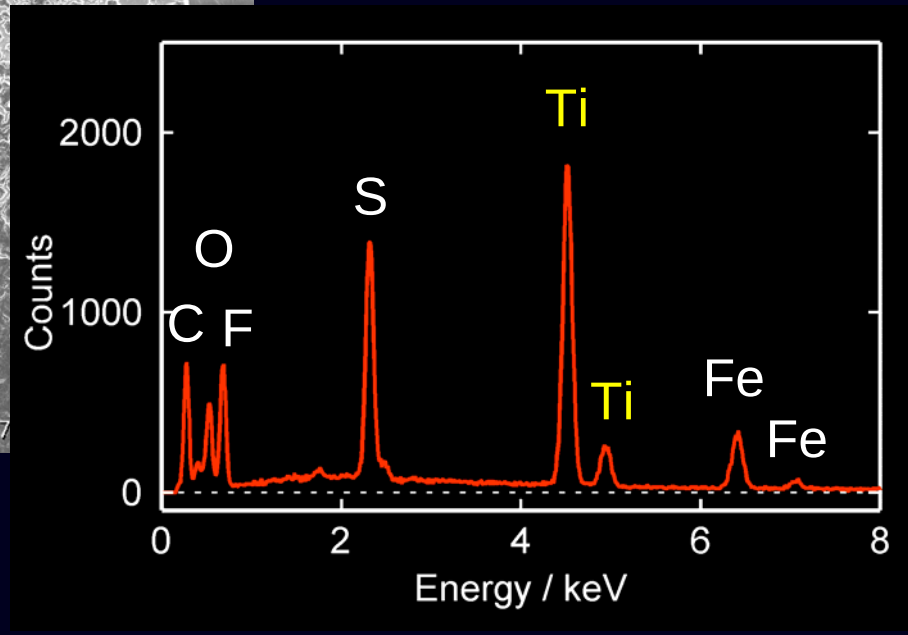
Lower part
(containing Ti ions)

Potentiostatic electrolysis at -2.7 V on Fe electrode.

SEM image

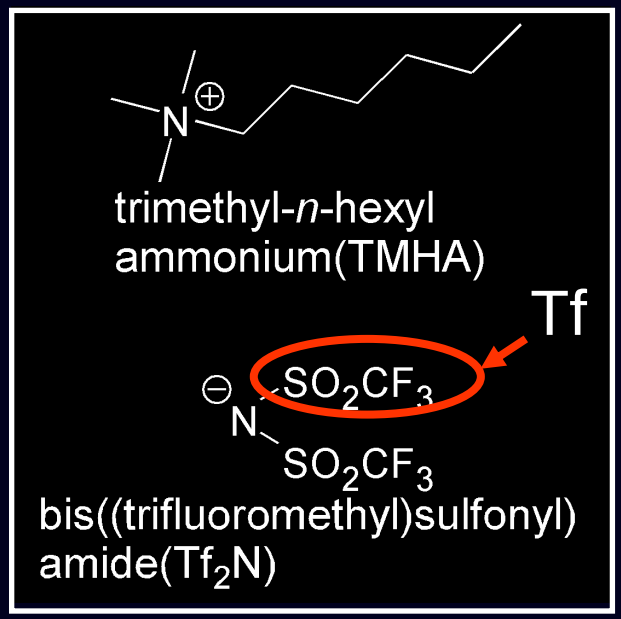


EDX analysis



The layer deposited on the surface contained titanium !!

Electrodeposition experiment



The layer was not metallic titanium.

Polymer may be formed by cathodic electrolysis.

ex.)

$$n\left[\begin{array}{c} Tf_2N \\ | \\ Tf_2N-Ti(II)-Tf_2N \\ | \\ Tf_2N \end{array}\right]^{2-} + 4n\,e = \left[\begin{array}{c} Tf \\ | \\ Ti(II) \\ | \\ Tf \end{array}\right]_n + 2n\,N_2 + 6n\,Tf^-$$

Conclusions

- Titanium electrode dissolves at high voltage with forming divalent or trivalent titanium ions in ionic liquid.
- Ionic liquid in anodic room separate into two parts by anodic decomposition. And titanium ions contain in lower part.
- The cathodic peaks at about -0.1 V and -1.2 V are observed when cyclic voltammetry is carried out in the ionic liquid containing titanium ions. There might be reduction of the decomposition products of ionic liquid.
- Titanium ions and a part of ionic liquid may form polymer by cathodic reaction of ionic liquid containing titanium ions.