Electrochemical Behavior of Titanium Electrode in TMHA-Tf_2N, Room Temperature Molten Salt

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Introduction

Electroplating of Titanium

Titanium has an ecellent corrosion resistance, as it forms a strong passive film. However, the application of bulk titanium material is limited because it costs so much to refine from ore.

→ Electroplating of titanium layer on a common metal surface is very attracive.

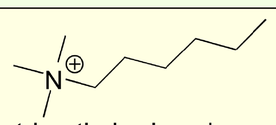
But it is almost impossible to electrodeposit titanium from aqueous media because of its largely negative redox potential. The standard electrode potential of titanium is the same as that of aluminum and much less than that of hydrogen.
In recent years, room temperature molten salts (ionic liquids) have been developed as an electrolyte for the deposition of base metals.

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

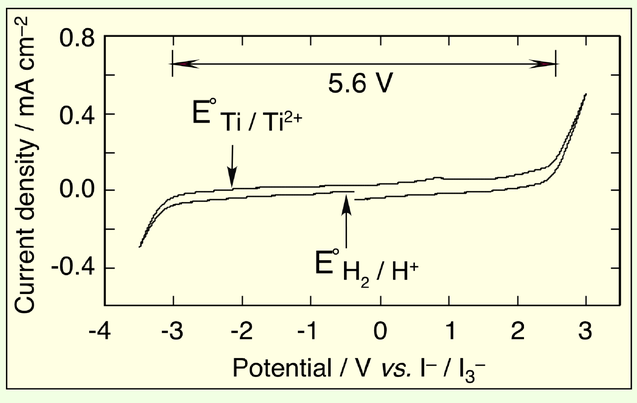
Electroplating titanium by room temperature molten salt at room temperature.

Room temperature molten salt (ionic liquids), "TMHA-Tf_2N"



trimethyl-*n*-hexyl ammonium(TMHA)

bis((trifluoromethyl)sulfonyl) amide(Tf_2N)



Wide electrochemical window · Ease of synthesis · Hydrophobic character

Why anodic dissolution?

There is no reported titanium salt which can be dissolved in TMHA-Tf_2N.

→ To feed titanium ion into TMHA-Tf_2N by anodic dissolution of a titanium electrode

Reason 1. It is easy to estimate the solubility of the titanium compounds combined with some anion in TMHA-Tf_2N.

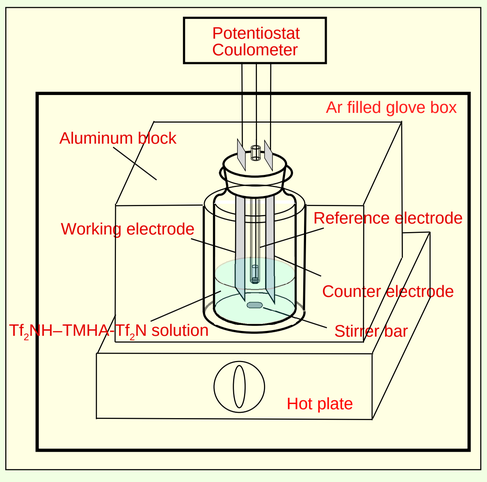
Reason 2. There is not enough margin between reductive decomposition potential of TMHA-Tf_2N and standard electrode potential of Ti^0/Ti^{2+}. However, there is enough margin between oxidative decomposition of TMHA-Tf_2N and standard electrode potential of Ti^0/Ti^{2+}.

Reason 3. The kinetics of electrochemical dissolution of metals are similar to that of electro-chemical deposition.

The purpose of this reserch

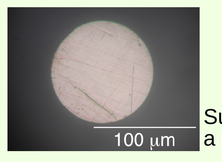
Investigating the anodic dissolution behavior of a titanium electrode in TMHA-Tf_2N.

Experimental



Bath — 50 mM Tf_2NH–TMHA-Tf_2N solution

Working electrode — Titanium, platinum, or platinum micro-disk electrode



Surface image of a platinum micro-disk electrode

Counter electrode — Titanium or platinum

Reference electrode — A platinum wire immersed in 15 mM I_2–60 mM $(n\text{-}C_3H_7)_4$ NI–TMHA-Tf_2N solution

$I_3^- + 2e \leftrightarrow 3I^-$

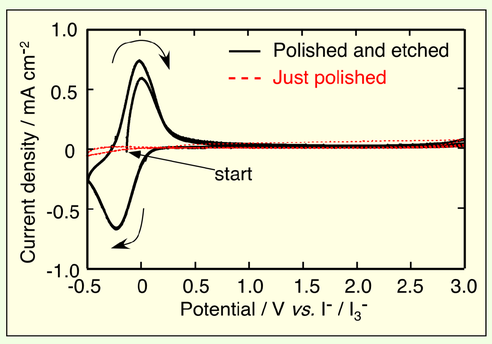
Results

The redox reaction at around -0.15 V vs. I^-/I_3^-

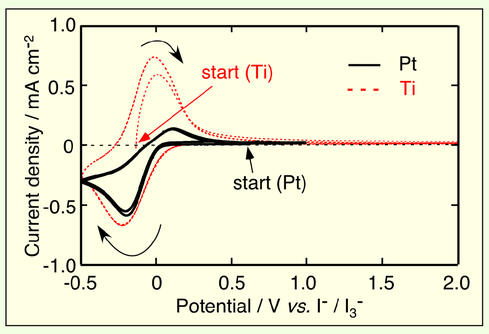
Cyclicvoltammograms on a titanium electrode

A set of large anodic and cathodic current of more than 0.5 mA cm^{-2} was observed at around -0.15 V *vs.* I^-/I_3^-.

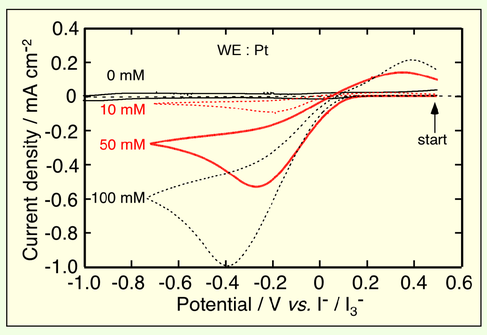
This reaction related to the redox of proton, which was added in the bath to avoid the reductive decomposition of TMHA-Tf_2N.



Cyclic voltammograms on a platinum electrode



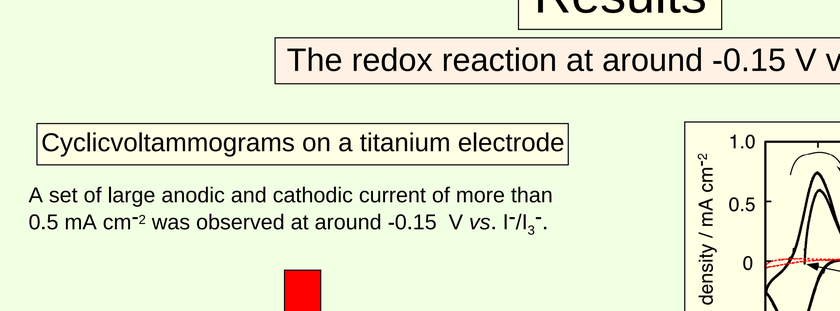
Dependence of cathodic current density on proton concentration



The redox reaction at around -0.15 V vs. I^-/I_3^- on platinum electrode

$2H^+ + 2e \leftrightarrow H_2$

Surface analysis of a titanium electrode by GD-OES (a) Before etching (b) After etching



Ti-H phase diagram

Y.Fukai, "From metal hydride to the ,etal hydrogen system," *J.Less-Common Metals*,172 (1991), 8-19

The redox reacton at around -0.15 V vs. I^-/I_3^- on a titanium electrode

$Ti + xH^+ + xe \leftrightarrow TiH_X$

Protonic diffusion coefficient in TMHA-Tf_2N

Linear sweep voltammograms

Potentiostatic electrolysis at -1.0 V

$$I_L = 2\pi nFC_{H^+}D_{H^+}a$$

I_L : Diffusion limiting current — n : Number of electrons
F : Faraday constant — C_{H^+} : Concentration of proton
D_{H^+} : Protonic diffusion coefficient — a : Radius of a micro-disk electrode

Protonic diffusion coefficient (10^{-7} cm^2 s^{-1})

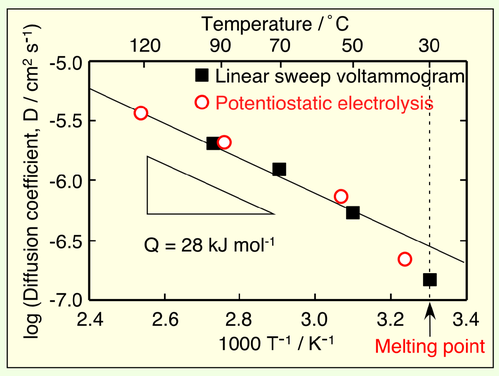
Temperature (℃)	30	50	70	90	120
Linear sweep volutammetory	2	5	12	21	
Potentiostat electrolysis	2	7		21	37

There is no difference in diffusion coefficient between protons and copper(I) (6 ×10^{-7} cm^{-2} s^{-1} at 50 °C*) in TMHA-Tf_2N.

→ Protons migrate not via Grotthuss mechanism but via Stokes mechanism in TMHA-Tf_2N.

* T. Katase, K. Kuniaki, T. Hirato, and Y. Awakura, *J.Appl.Electrochem.*, in press.

Arrhenius plot



Conclusions

The redox reaction observed at around -0.15 V vs. I^-/I_3^- on the etched titanium electrode was follows.

$$Ti + xH^+ + xe \leftrightarrow TiH_X$$

The protonic diffusion coefficient in TMHA-Tf_2N was calculated.
The value is 5~7 × 10^{-7} cm^2 s^{-1}. It is as same as that of Cu^+.