Electrochemical Behavior of Titanium Electrode in TMHA-Tf₂N, Room Temperature Molten Salt

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Introduction

Electroplating of Titanium

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

Electroplating of titanium layer on a common metal surface is very attractive. The redox reaction at around -0.15 V vs. I-/I₃⁻ on a titanium electrode was follows.

\[ 2H^+ + 2e^- \rightarrow H_2 \]

However, there is enough margin between oxidative decomposition of TMHA-Tf₂N and standard electrode potential of Ti/TiH₂. However, there is enough margin between oxidative decomposition of TMHA-Tf₂N and standard electrode potential of Ti/TiH₂.

Why anodic dissolution?

There is no reported titanium salt which can be dissolved in TMHA-Tf₂N. To feed titanium ion into TMHA-Tf₂N 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-Tf₂N.

Reason 2. There is not enough margin between reductive decomposition potential of TMHA-Tf₂N and standard electrode potential of Ti/TiH₂.

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

The purpose of the research

Investigating the anodic dissolution behavior of a titanium electrode in TMHA-Tf₂N.

Experimental

50 mM Ti(NH₄)₂TMHA-Tf₂N solution

Titanium or platinum

A platinum wire immersed in 15 mM NH₄F-Tf, Ni-TMHA-Tf₂N solution

Reference electrode

Hot plate

Stirrer bar

Working electrode

Counter electrode

Bath

Linear sweep voltammograms

Potentiostatic electrolysis at -1.0 V

Protonic diffusion coefficient in TMHA-Tf₂N

Protonic diffusion coefficient in TMHA-Tf₂N solution

And standard electrode potential of Ti/TiH₂

Potentiostatic electrolysis at -1.0 V

There is no difference in diffusion coefficient between protons and copper(I) (6 × 10⁻⁷ cm² s⁻¹ at 50 °C) in TMHA-Tf₂N.

Protons migrate not via Grotthuss mechanism but via Stokes mechanism in TMHA-Tf₂N.

Conclusions

The redox reaction observed at around -0.15 V vs. I_/I₃⁻ on the etched titanium electrode was follows.

Ti + xH⁺ + xe⁻ = TiHₓ

The protonic diffusion coefficient in TMHA-Tf₂N was calculated.

The value is 5–7 × 10⁻⁷ cm² s⁻¹. It is as same as that of Cu⁺.