Selective reduction of actinyl ions based on electrocatalysis using platinized glassy carbon fiber column electrode

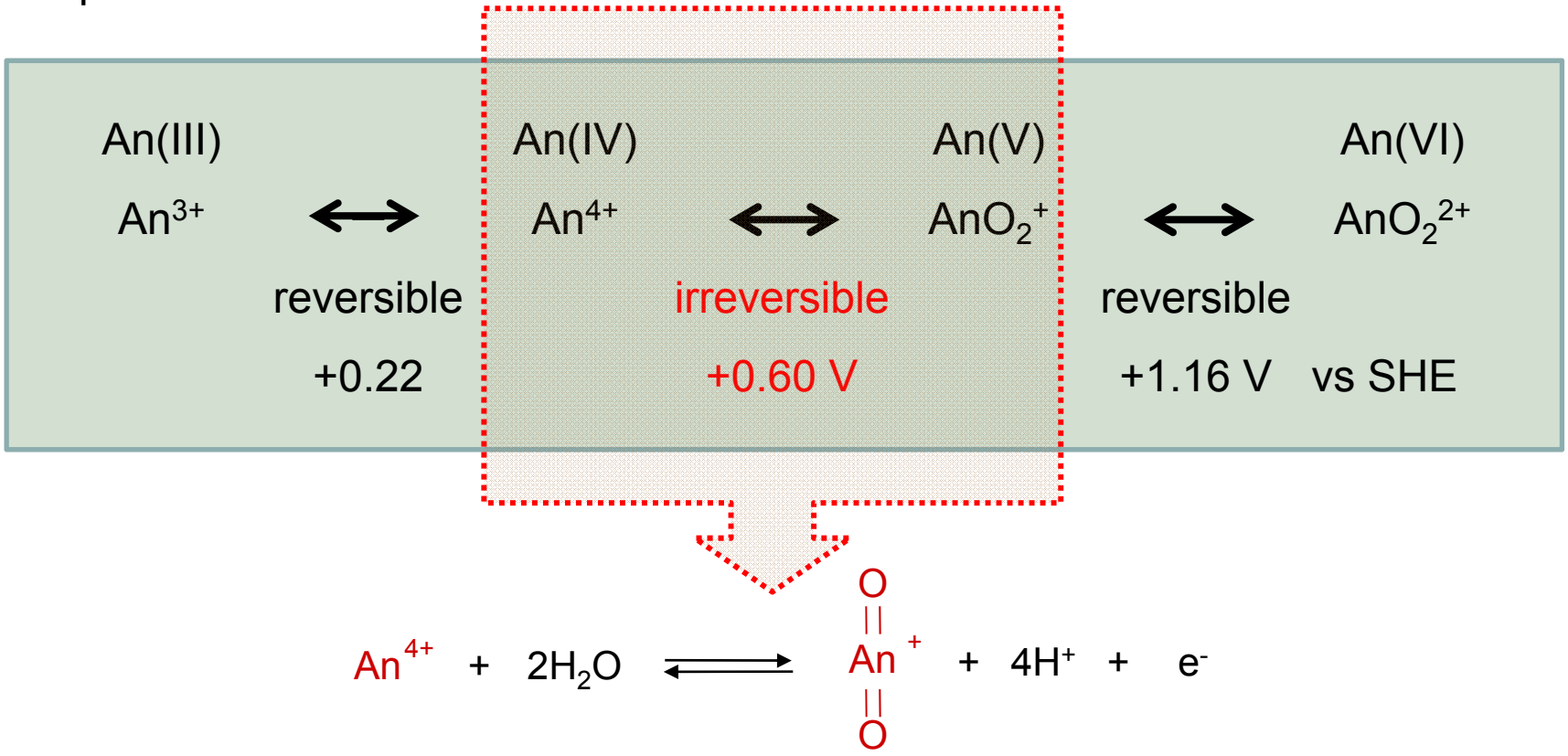
Yoshihiro Kitatsuji[1], Takaumi Kimura[1], Sorin Kihara[2]

[1] Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency
[2] Kyoto Institute for Interesting Chemistry

Redox reaction of actinide ions by electrolysis

Adjustment of the oxidation state of U, Np and Pu ions inevitable for the

- efficient chemical separation
- precise determination

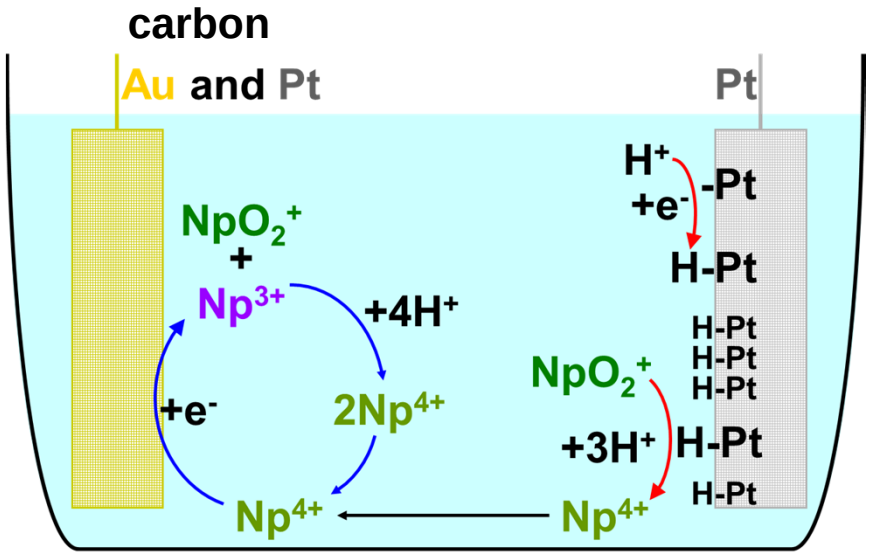


The irreversibility of the redox of An(IV)/(V) comes from the formation or decomposition of actinyl ions.

Two Reduction Schemes of NpO_2^+ during Electrolysis

NpO_2^+ is reduced by electrolysis through

- Chemical reaction coupled with Np^{4+}/Np^{3+} electrode reaction as an electron transfer mediator
- Electrocatalytic reduction by the hydrogen atom adsorbed on the Pt electrode, Pt-H_{ads}



Pt electrode is good electrode catalyst for reduction of Np(V).

Y. Kitatsuji, et al., J. Electroanal. Chem. 641 (2010) 83.

Aims of this study

Flow electrolysis with column electrode of glassy carbon (GC) fiber
Rapid electrolysis method for controlling oxidation state of actinide ions

Electrode catalyst of Pt
to decrease overpotential

Flow electrolysis with platinized GC fiber electrode
Redox of U, Np and Pu

Selective preparation of oxidation state of actinide ions

Column electrode with glassy carbon fiber working electrode

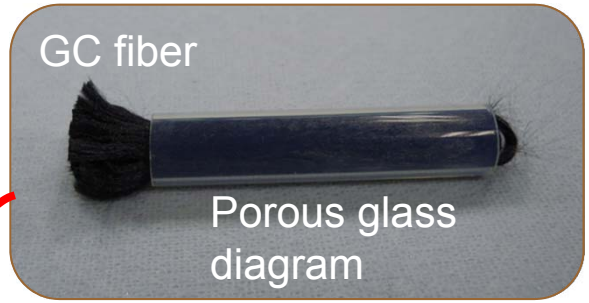
The column electrode

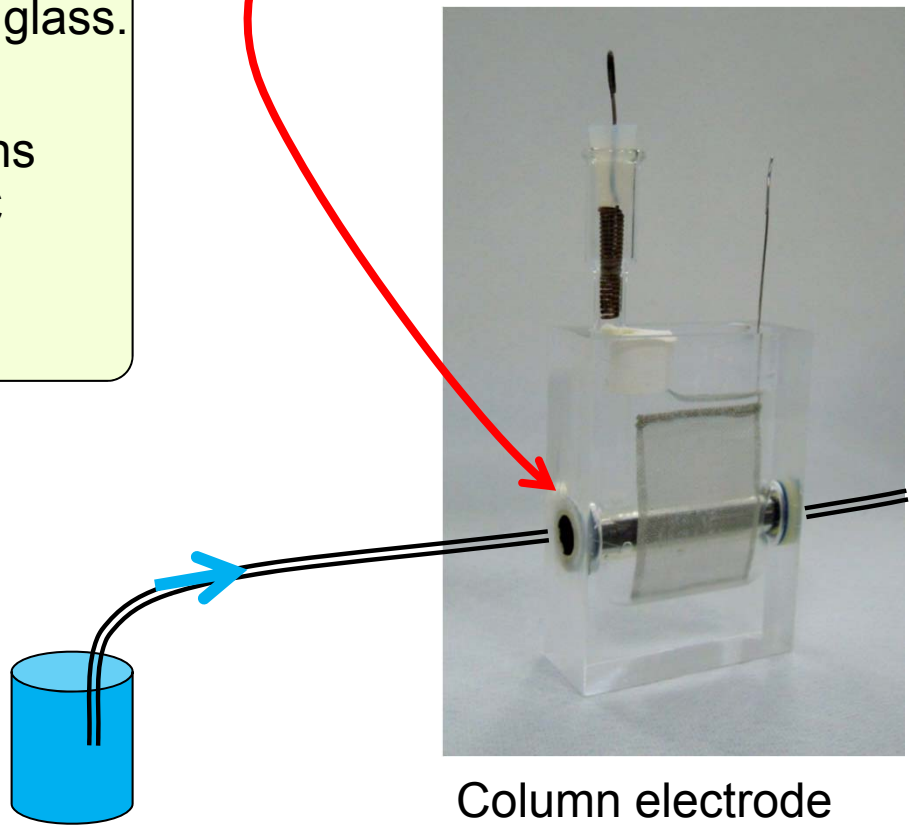
working electrode: a bundle of very thin GC fibers packed tightly in a cylindrical electrolytic diaphragm cell of porous glass.

The flow electrolysis: passing the electrolyte solution containing the ions through the narrow paths among GC fibers.

- Rapid
- Quantitative
- High sensitivity
- Multiple electrolysis

Platinization of GC fiber:
by electrodeposition





Column electrode

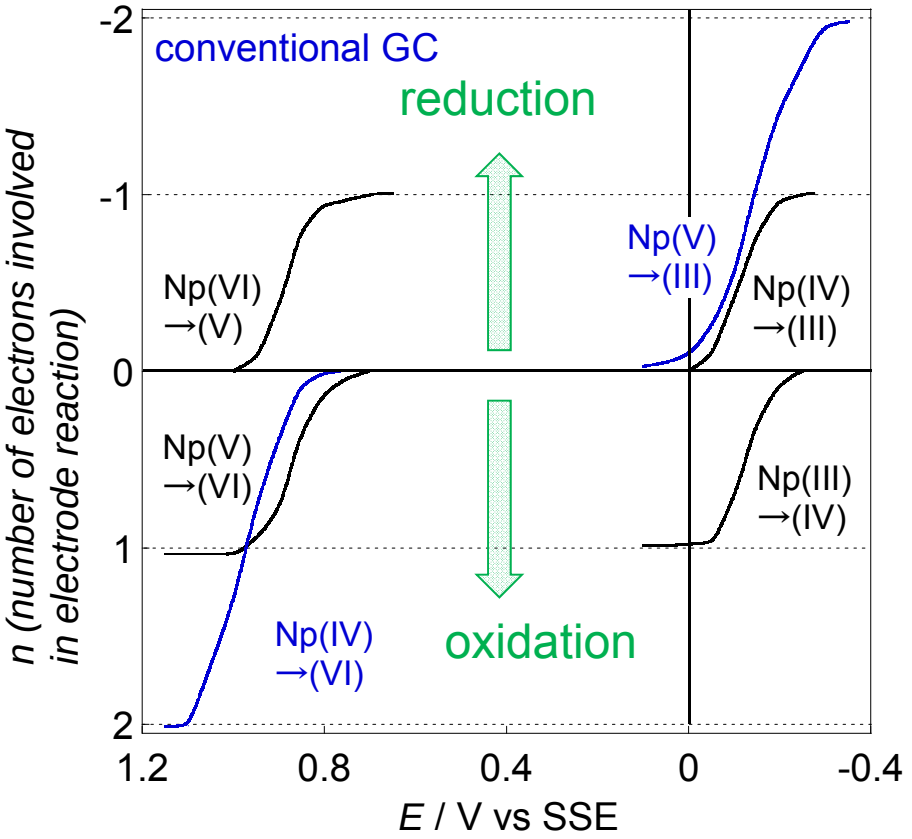
Redox of Np at **normal GC** column electrode electrolysis

$I = nFfc$

- I: current
- n: number of electrons involved in electrode reaction
- F: the Faraday constant
- f: flow rate of sample solution
- c: concentration of the ion

Np(III) / Np(IV)
Np(V) / Np(VI)
- Reversible

Np(IV) / Np(IV)
- Irreversible
- Large overpotential



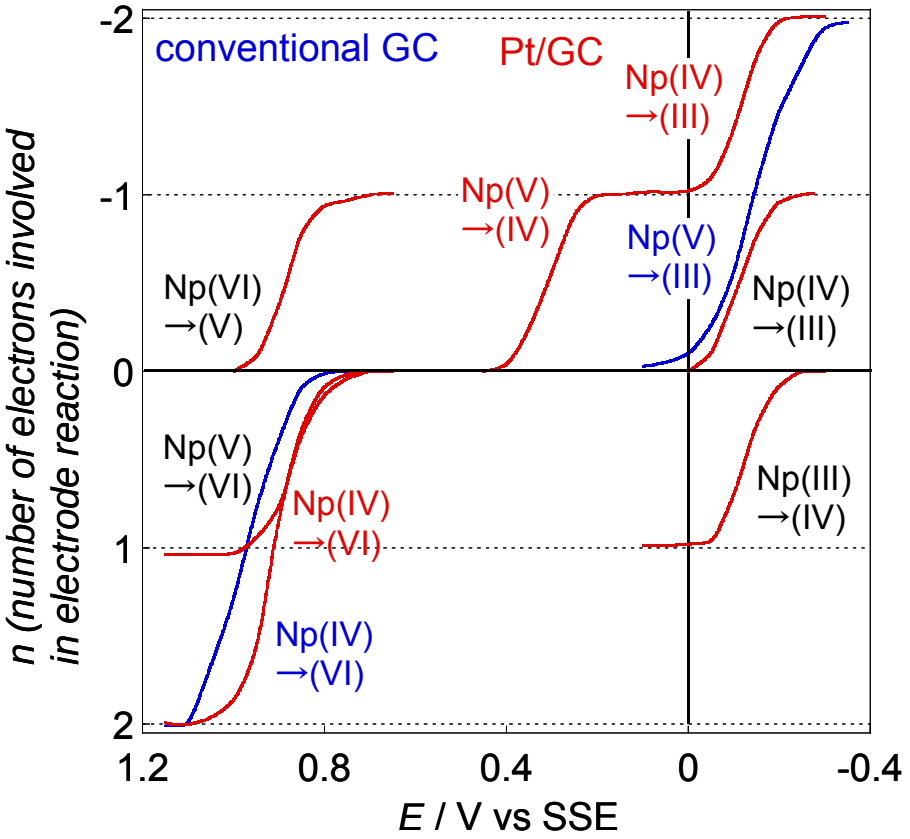
Coulopotentiogram (current-potential relation) of redox of Np ions measured with column electrode.
Solution: 1mM Np + 1M $HClO_4$.

Redox of Np at **Pt/GC** column electrode electrolysis

Reduction of Np(V)
- successive wave
- Np(V) → Np(IV) → Np(III)

Oxidation of Np(IV)
- 2-electron wave
- Np(IV) → Np(VI)
- ca. 0.1V shift negatively

Np(III) / Np(IV)
Np(V) / Np(VI)
- Reversible
- Same redox potentials



Coulopotentiogram (current-potential relation) of redox of Np ions measured with column electrode.
Solution: 1mM Np + 1M $HClO_4$.

Redox of Pu at Pt/GC column electrode electrolysis

Reduction of Pu(VI) ion

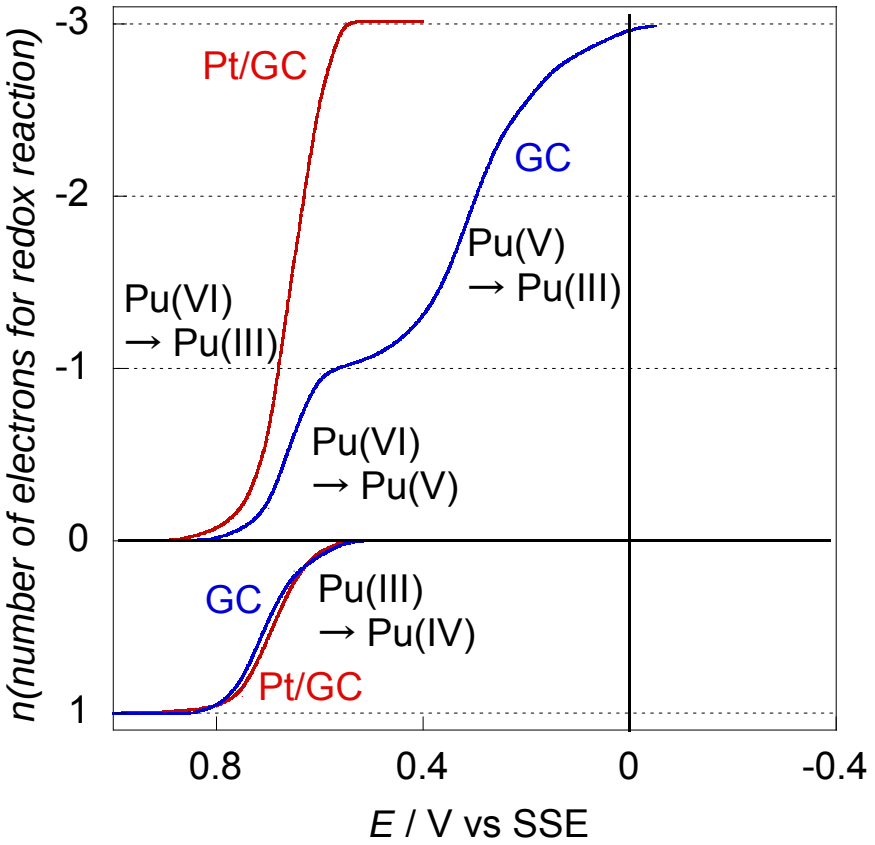
GC: two reduction waves
Pu(VI) → Pu (V)
Pu(V) → Pu (III)

Pt/GC: One-step reduction wave
Pu(VI) → Pu(III)

E^0 of Pu(III)/(IV): +0.72 V
E^0 of Pu(V)/(VI): +0.78 V

Oxidation of Pu(III)
independent on electrode materials.

Oxidation of Pu(IV)
Not observed



Coulopotentiogram of redox of Pu ions measured with column electrode.
Solution: 1mM Pu + 1M $HClO_4$.

Redox of U at Pt/GC column electrode electrolysis

Reduction of UO_2^{2+} to U^{4+}

- One-step two-electron reduction
- Little affected by working electrode materials.
- Reduction potentials are almost same.

$UO_2^{2+} + 2e^- + 4H^+ \rightarrow U^{4+} + 2H_2O$

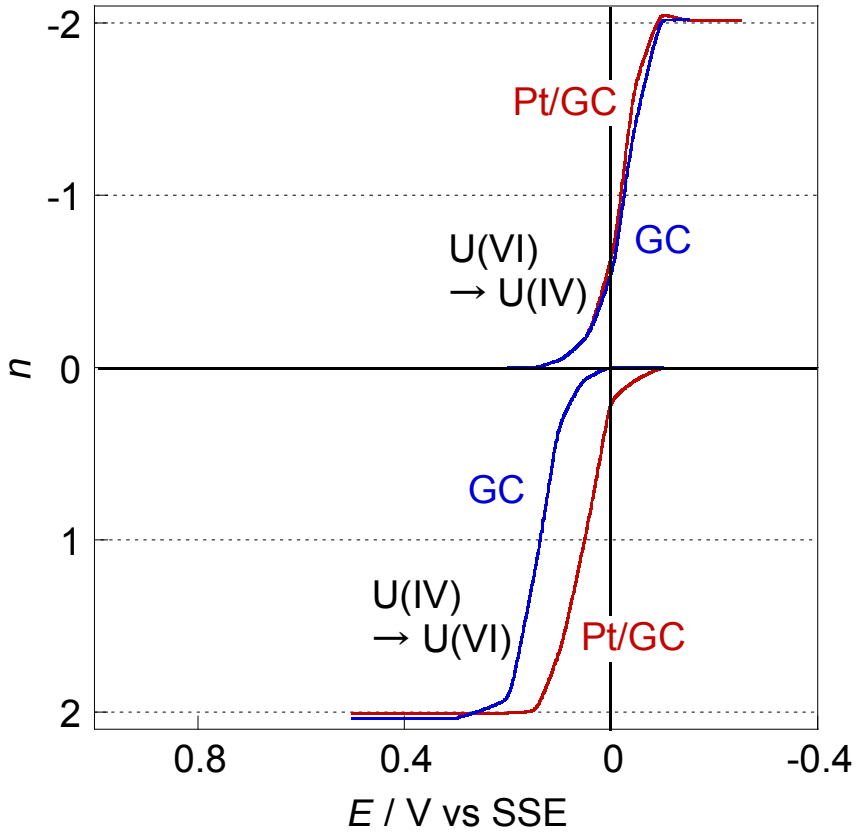
Elementary reactions:

$UO_2^{2+} + e^- \rightarrow UO_2^{+}$ (reversivble)

$2UO_2^{+} + 4H^+ \rightarrow U^{4+} + UO_2^{2+} + 2H_2O$

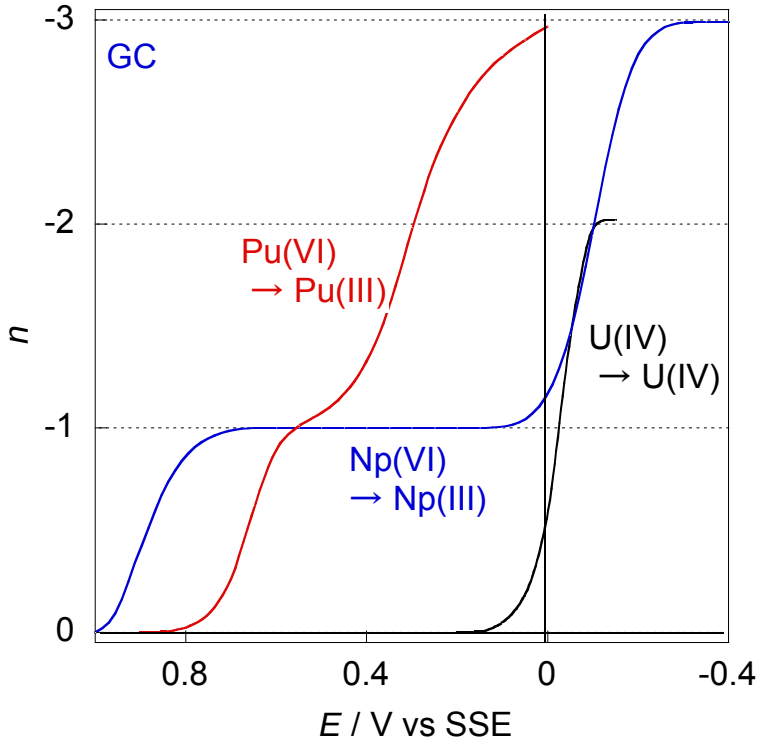
Oxidation of U^{4+} to UO_2^{2+}

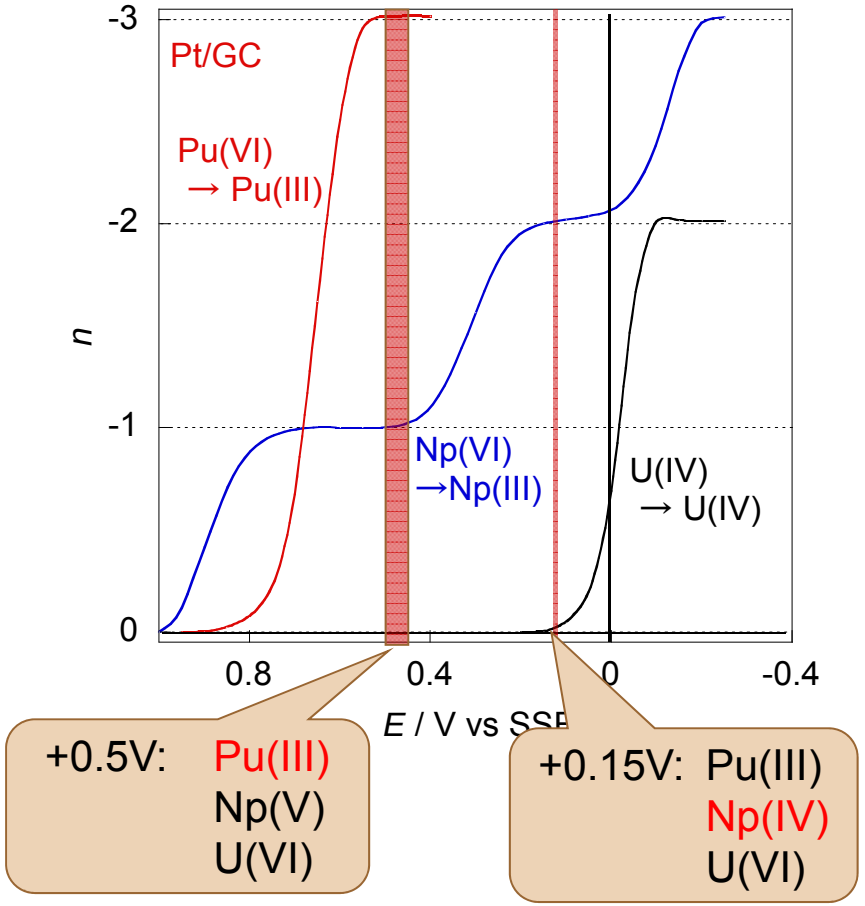
- One-step two-electron oxidation
- shifts about 0.1 V to negative potential at Pt/GC electrode.



Coulopotentiogram of redox of U ions measured with column electrode.
Solution: 1mM U + 1M $HClO_4$.

Control of oxidation states of Np or Pu by selective reduction





Conventional method（GC fiber WE)

- Large overpotential
- One step reduction of Np(V) to Np(III)

→Difficult to selective preparation of oxidation states

- Np(IV) can be prepared from Np(III), Np(V) or Np(VI).
- Selective reductions to Pu(III) and Np(IV) are possible.

Conclusions

Employing platinized electrode enables to mitigate the overpotential of Np(V) and Pu(V) reductions effectively.

The flow-electrolysis with Pt/GC permits the selective preparations of Np(IV) and Pu(III).

This electrocatalytic reduction is very useful to control the oxidation states of An ions also in the mixture solution of U, Np and Pu.