

Supporting Information

How Plutonium “Brown” Peroxo Complex emerges from Aerated Electrolysis Experiments

Richard Husar, Quentin Hervy, Thomas Dumas,* Philippe Guilbaud, Matthieu Virot and Philippe Moisy

S.I. 1: Experimental setup for *in situ* experiments

Spectroelectrochemical UV-vis/NIR setup: An optical micro-cell (Figure S1.) with quartz windows was developed in-house and installed into a glovebox system connected to a Cary 6000 Spectrometer by fiber optics and with a Metrohm Potentiostat. The micro-cell consists of an optical reaction compartment (path length: 20 mm; min./max. analytical volume: 750/1800 μ l) and a cell cap coupling electrodes and electronic connection, both manufactured out of inert VESPEL™ (DuPont) material. The optical reaction compartment was designed to facilitate homogenization of bulk solution by magnetic stirring without impacting electrochemical conditions and online measurement of electronic absorption during electrolysis without effects due to electrode material within the optical path/window.

Working / counter Platinum electrodes by Biologic, reference Ag/AgCl (World Precision Instruments), Counter-electrode additionally separated within the reaction compartment by diaphragm by metrohm; micro stirrer.

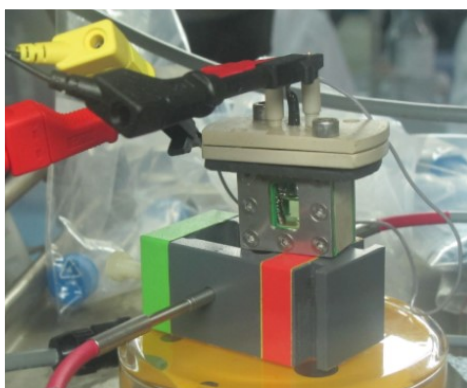


Figure S1: Spectroelectrochemical micro-cell with optical fibers and electronic connections.

S.I. 2: Purified plutonium oxidation states plutonium spectra used as references for spectral deconvolution and associated molar absorptivity and table of molar absorptivity of the main Pu redox species.

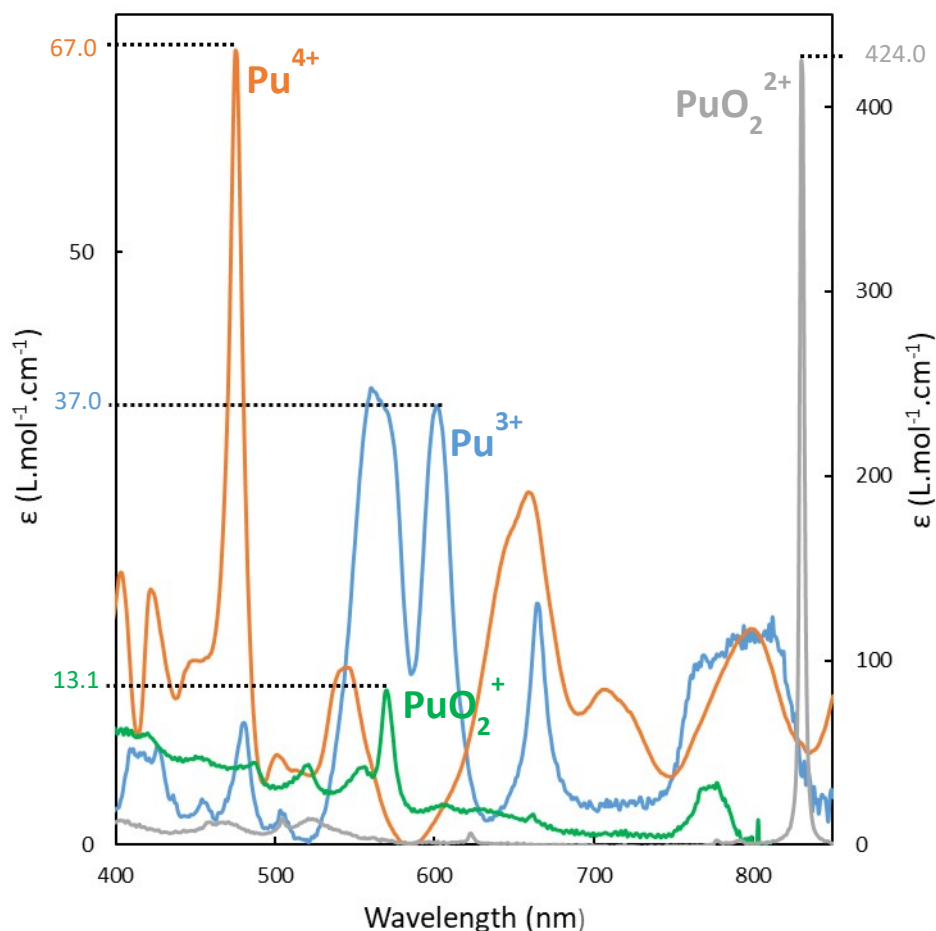


Figure S2: UV-vis/NIR absorption spectra of isolated Pu oxidation states as a function of the applied potential in solution (vs ESH.): a) Pu(VI) at (+)810 mV (grey), b) Pu(V) at (+)550 mV (green), c) Pu(III) at (-)100 mV (blue) and d) Pu(IV) at (+)800mV (orange). The order from top to bottom reflects the stepwise oxidation state isolation sequence starting from a) initial Pu(VI)

Table S1. Molar absorptivity of Pu redox species in nitric acid solution (0.1 M HNO₃)

Species		Absorption peak - this work -		J.F Wagner <i>et al.</i> ¹	
Ion	Oxidation state	Wavelength [nm]	Molar absorptivity [M ⁻¹ cm ⁻¹]	Wavelength [nm]	Molar absorptivity [M ⁻¹ cm ⁻¹]
PuO ₂ ⁺	(V)	570	13.1	n.r.	n.r.
PuO ₂ ²⁺	(VI)	830	424.0	830	545
Pu ³⁺	(III)	602	37.0	602	38
Transient species (Air)	(IV)	496	~ 230	495*	266*
Pu ⁴⁺	(IV)	475	67.0	476	68

* References (Connick *et al.*), ~ to be further confirmed

S.I. 3: Deconvolution applied for the two transient species signal isolation

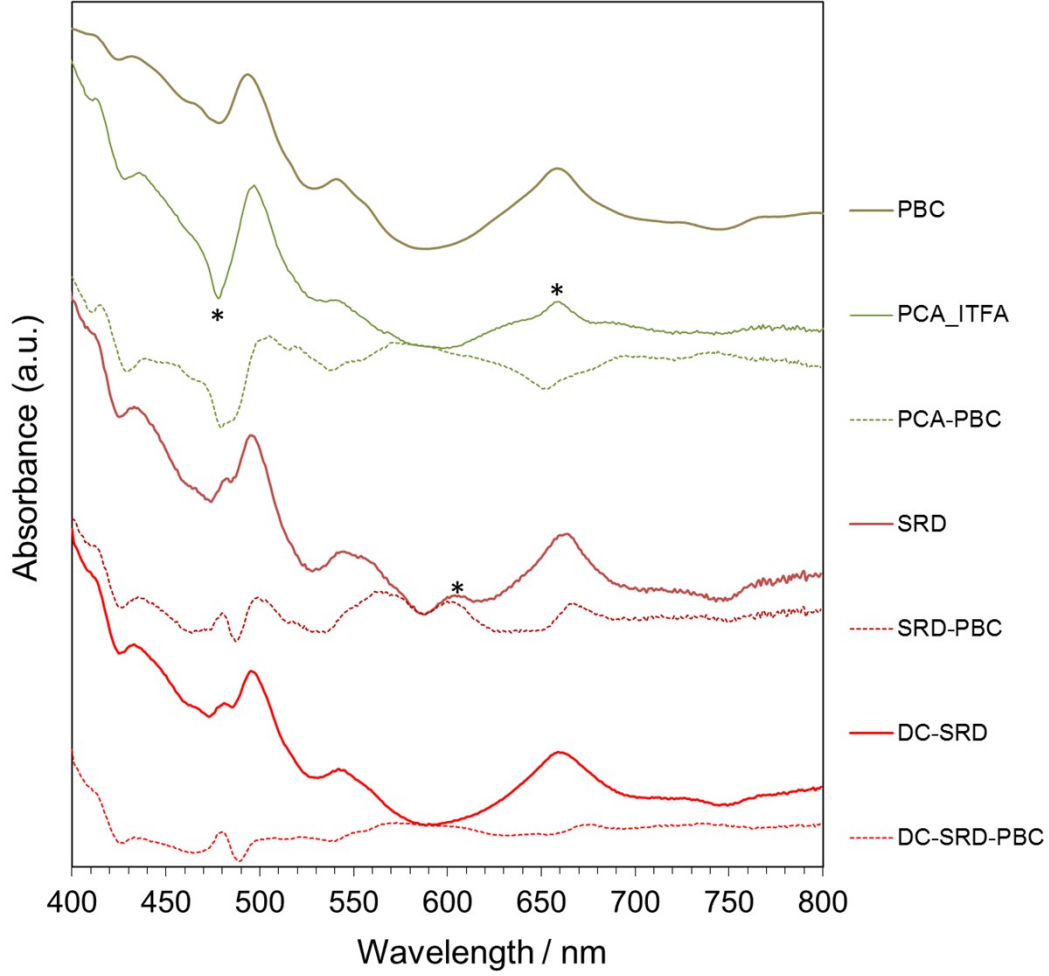


Figure S3: Comparison of transient species (Air) to the Pu “brown” complex spectrum

Transient species (Air) spectra was first obtained by conventional procedures of principal component analysis and iterative transformation factor analysis (S.I.3 green).² This procedure was applied using only principal components. (*) As a function wavelength range selected for deconvolution, the absorbance measured in UV-region for intermediate species enforced the deconvolution by the conventional PCA analysis (PCA-ITFA) to spuriously fluctuate the Pu(III) and Pu(IV) reference bands intensity in the resulting transient species (Air) spectra. Hence, after this first PCA deconvolution performed in 400nm – 800nm range, the transient species (Air) spectra was refined by a self-referencing procedure (SRD) based on the reference Pu(III), Pu(IV), Pu(VI), transient species (Argon) spectra and the first electrolysis. 8 and 4 spectra were acquired respectively for oxidation and reduction experiments. This procedure applies the following formula (Eq. S1 and Eq. S2):

$$A_{\lambda,n}^{TPI-2} = \sum_{n,\lambda} (A_{\lambda,n}^{exp} - c_n^{PuIV} A_{\lambda}^{PuIV} - c_n^{PuIII} A_{\lambda}^{PuIII} - c_n^{PuVI} A_{\lambda}^{PuVI} - c_n^{TPI-1} A_{\lambda}^{TPI-1}) \quad (S1)$$

$$A_{\lambda}^{TPI-2} = \sum_n (A_{\lambda,n}^{TPI-2} / (1 - c_n^{PuIV} - c_n^{PuIII} - c_n^{PuVI} - c_n^{TPI-1})) \quad (S2)$$

Where:

n is the nth spectrum in the electrolysis experiment

λ is the wavelength

$A_{\lambda,n}^{(PuIII, PuIV, TPI, exp)}$ is the absorption of the spectra n at a wavelength λ (respectively for Pu(III), Pu(IV), transient species (Argon), transient species (Air) or measured)

The final SRD spectra (S.I.3 brown) for the transient species (Air) is then determine by the optimization of the c_n^{PuIV} , c_n^{PuIII} , c_n^{PuVI} and c_n^{TPI-1} values to get equation S3:

$$\sum_{n,\lambda}^2 (A_{\lambda,n}^{TPI-2} - (A_{\lambda,n}^{exp} - c_n^{PuIV} A_{\lambda}^{PuIV} - c_n^{PuIII} A_{\lambda}^{PuIII} - c_n^{PuVI} A_{\lambda}^{PuVI} - c_n^{TPI-1} A_{\lambda}^{TPI-1})) \rightarrow 0 \quad (S3)$$

This procedure was applied for both reduction and oxidation experiments independently or in combination. A comparison of the resulting transient species (Air) spectra issuing from oxidization and reduction experiments is provided bellow. This confirms that the transient complex is the same in both experiments.

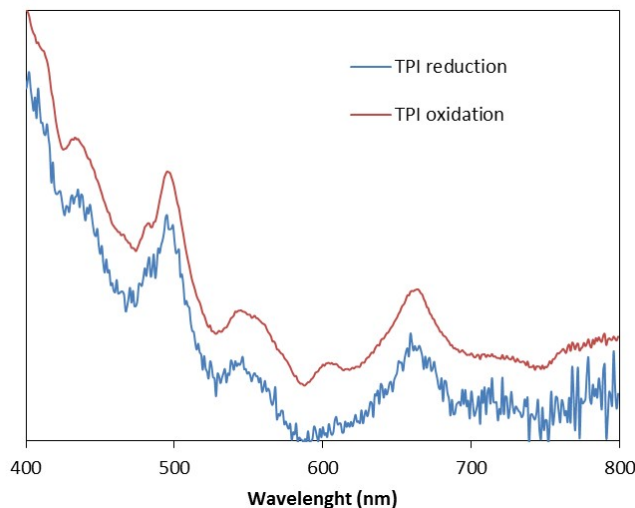


Figure S4: Comparison between the two **transient species (Air)** isolated by deconvolution for both oxidation and reduction

A second constrain was finely included in the SRD procedure to properly remove the references Pu(III), Pu(IV), Pu(VI) and transient species (Argon) signals from the resulting transient species (Air) spectra (S.I.2 red spectra). This constrain is made by excluding zero values for the transient species (Air) spectra derivative on the main references absorption bands. ($\lambda= 479$ nm, $\lambda= 602$ nm, $\lambda= 830$ nm, $\lambda= 462$, 482 nm and $\lambda= 657$, 681 nm). Interestingly, this deconvolution results in the spectra that is the more similar to the Pu-brown prepared independently from electrolysis.

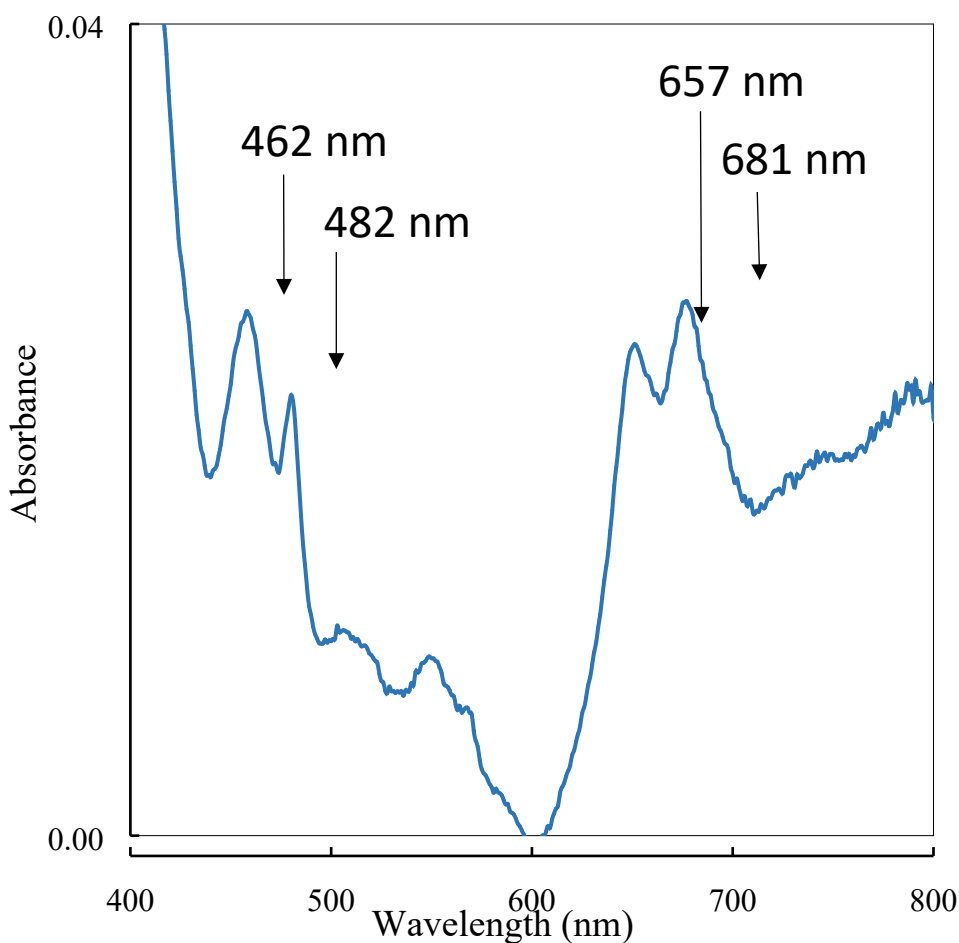


Figure S5: Isolate spectrum of the transient species (Argon) observed under argon atmosphere

The bands showed on the spectrum in Figure 3 are very similar to those observed by Cot-Auriol *et al.*³ who compared them to an oxo-hydroxo hexanuclear core of a Pu(IV) cluster decorated by acetate or DOTA ligands discovered by Tamain *et al.*⁴ Moreover, the small bands between 500 and 580 nm are also observed on the species isolated by Cot-Auriol *et al.* and by Tamain *et al.* These bands could be an other signature of the Pu(IV) cluster.

S.I. 4: Determination method of error bars for the plutonium speciation during electrolysis.

Given that the deconvolution is derived from on a self-referencing procedure that assumes exact mass balance and minimizes errors in the whole wavelength range to create the transient species spectra, we used a single method to provide error bars. This method remains approximate and should be considered with caution, but gives maximized error bars: Considering a continuous recording during electrolysis, each concentration point is determined for a changing solution and must be assumed to lie at least between the previous and the next concentration point. Thus, the positive error bar for each concentration is calculated as the difference between the previous concentration and the one for which the uncertainty is being evaluated. For the negative error bar, it is the difference between the concentration being evaluated and the next one.

REFERENCES

- (1) Wagner, J.-F.; Vian, A. Analyse de l'uranium et des éléments transuraniens. **1999**. Connick, R. E.; Kasha, M.; McVey, W. H.; Sheline, G. E.; *Commission, U. S. A. E.; Technical Information Division, Oak Ridge Operations: 1946*, 559; cHagan, P. G.; Miner, F. J. U.S. Atomic Energy Commission Golden, Colorado, **1969**; 1-10; dHall, G. R.; Herniman, P. D.; Walter, A. J. Atomic Energy Research Establishment (AERE): Harwell, **1951**; e Myers, M. N. U.S. Atomic Energy Commission: Richland, Washington, **1956**; p 22.
- (2) aC. Lucks, A. Rossberg, S. Tsushima, H. Foerstendorf, A. C. Scheinost, G. Bernhard, *Inorg Chem* **2012**, *51*, 12288-12300; bA. Rossberg, T. Reich, G. Bernhard, *Analytical and bioanalytical chemistry* **2003**, *376*, 631-638; cT. Watanabe, Y. Ikeda, in *3rd International Conference on Asian Nuclear Prospects, Vol. 39* (Eds.: J. Chen, X. Liu, S. Li, G. Ye), Elsevier Science Bv, Amsterdam, **2013**, pp. 81-95.
- (3) Cot-Auriol, M.; Virot, M.; Dumas, T.; Diat, O. First Observation of [Pu₆(OH)₄O₄]₁₂₊ Cluster during the Hydrolytic Formation of PuO₂ Nanoparticles Using H/D Kinetic Isotope Effect. *The Royal Society of Chemistry*. **2022**.
- (4) Tamain, C.; Dumas, T.; Guillaumont, D.; Hennig, C.; Guilbaud, P. First Evidence of a Water-Soluble Plutonium(IV) Hexanuclear Cluster. *Eur. J. Inorg. Chem.* **2016**, *2016* (22), 3536–3540. <https://doi.org/10.1002/ejic.201600656>.

