SUPPORTING INFORMATION

Insights for Controlling Plutonium Behavior in Hydrochloric Acid Solutions

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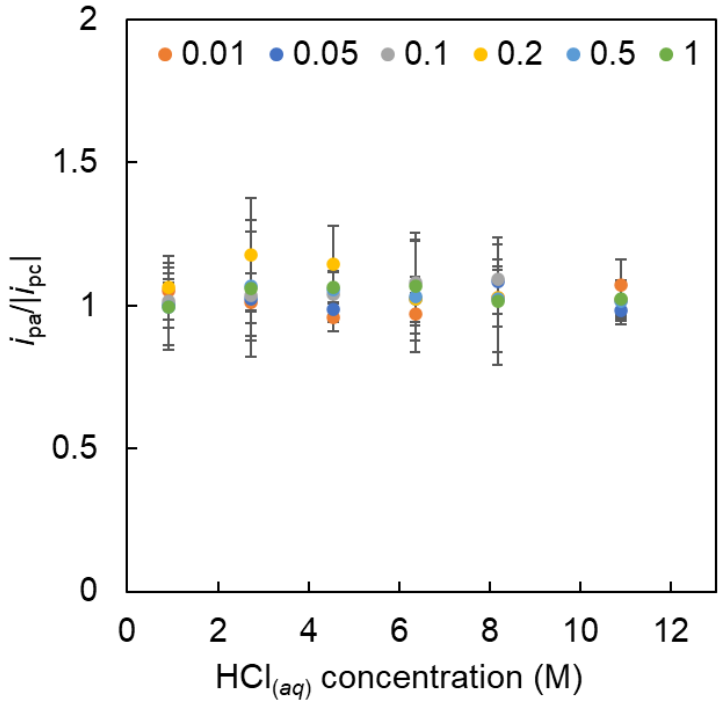

Figure S1. Dependence of the ratio of anodic peak current, i_{pa}, to cathodic peak current, i_{pc}, on the $HCl_{(aq)}$ concentration at different scan rates (0.01 – 1 V/s), represented by orange (0.01), blue (0.05), gray (0.1), yellow (0.2), cyan (0.5), and green (1 V/s), respectively.

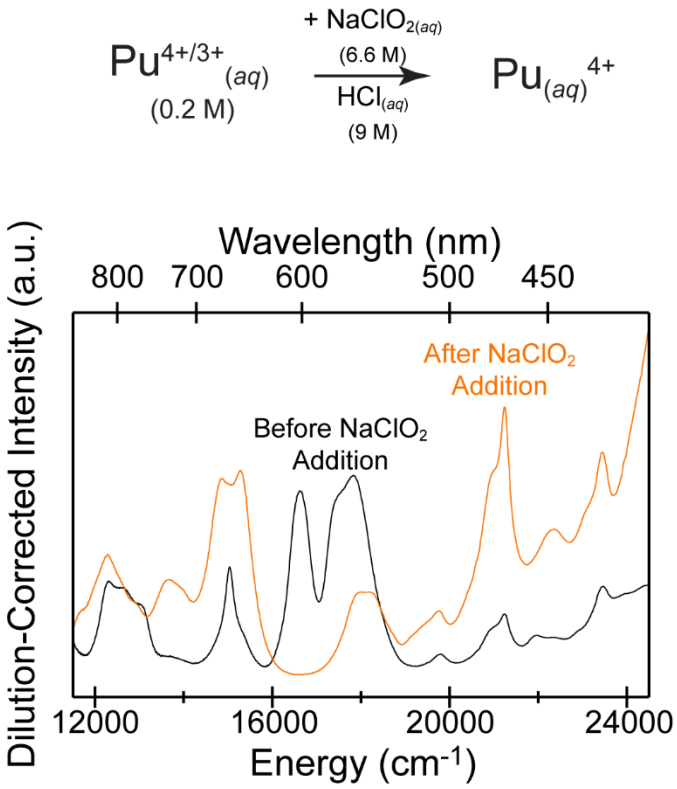

Figure S2. The UV-Vis-NIR spectra from plutonium solutions (0.2 M) dissolved in $HCl_{(aq)}$ (9 M) before (black trace) and after (orange trace) additions of $NaClO_{2(aq)}$ (6.6 M). Before $NaClO_{2(aq)}$ addition, the UV-Vis-NIR spectrum showed a mixture of $Pu^{4+}{}_{(aq)}$ and $Pu^{3+}{}_{(aq)}$. After $NaClO_{2(aq)}$ addition, only $Pu^{4+}{}_{(aq)}$ was detected.

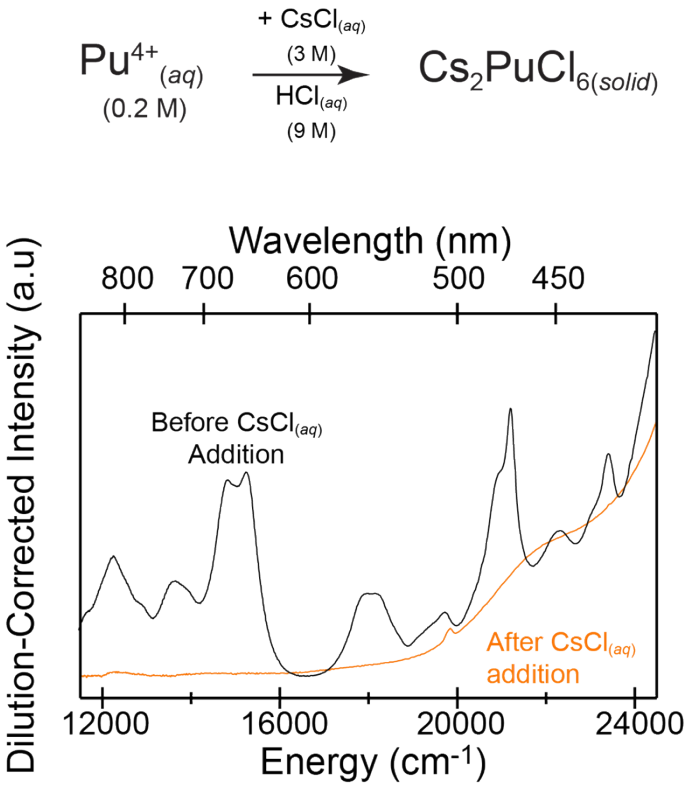

Figure S3. The UV-Vis-NIR spectra from a $Pu^{4+}_{(aq)}$ (0.2 M) solution dissolved in $HCl_{(aq)}$ (9 M) before (black trace) and after (orange trace) additions of $CsCl_{2(aq)}$ (3 M). Before $CsCl_{(aq)}$ addition, the UV-Vis-NIR spectrum showed $Pu^{4+}_{(aq)}$ dissolved in solution. Addition of $CsCl_{(aq)}$ caused the plutonium the precipitate as $Cs_2PuCl_{6(solid)}$.

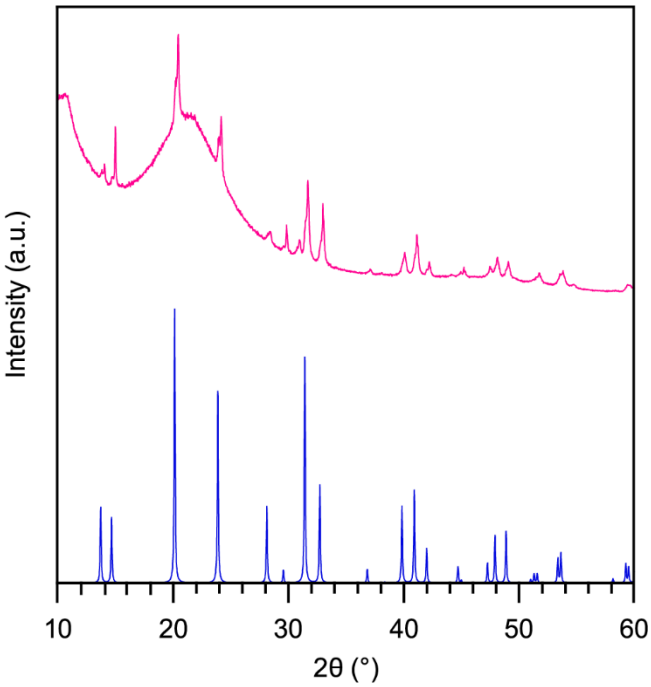

Figure S4. The PXRD patterns of the as-prepared $Cs_2PuCl_{6(solid)}$ (pink trace) compared to the simulated PXRD pattern (blue trace) from the reported crystal structure.[1] The simulated pattern was made in Mercury.[2]

Table S1. The coefficient of determination, R^2, for the least-squares fitting of peak current (i_p) as a function of the scan rate ($v^{1/2}$) for plutonium in $HCl_{(aq)}$ solutions (1 – 11 M).

	Pu $HCl_{(aq)}$ Solutions				
	1 M $HCl_{(aq)}$	**3 M $HCl_{(aq)}$**	**5.5 M $HCl_{(aq)}$**	**8 M $HCl_{(aq)}$**	**11 M $HCl_{(aq)}$**
R^2	0.996	0.988	0.987	0.992	0.995

II. Equation Derivations

Using Halfwave Potentials ($E_{½}$) to Evaluate Pu Coordination Numbers for Cl^{1-}.

The $Pu^{4+/3+}$ electron transfer in $HCl_{(aq)}$ solutions at low scan rates was best described as a reversible redox process (Eq 1) coupled with reversible complexation reactions (Eq 2). This means that the half-wave potentials ($E_{½}$) dependence on $HCl_{(aq)}$ concentration inform on the number of Cl^{1-} ligands (symbolized by *l*) bound by $Pu^{4+}{}_{(aq)}$. A mathematical expression (Eq 5) can be derived to infer the ligand number with the aid of chemical equilibrium (Eq 2), Nernst equation (Eq 3), and steady-state mass transport equation (Eq 4).[3]

$$Pu^{4+} \rightleftharpoons Pu^{3+} \qquad \text{Eq 1}$$

$$Pu^{4+} + x \cdot Cl^{-} \overset{K}{\rightleftharpoons} PuCl_{x}^{4-x} \qquad K = \frac{C_{PuCl_x}}{C_{Pu^{4+}} C_{Cl^-}^{x}} \qquad \text{Eq 2}$$

$$E = E^{o} - \frac{RT}{nF}\ln\frac{a_{Pu^{3+}}}{a_{Pu^{4+}}} = \underbrace{E^{o} - \frac{1}{nf}\ln\frac{\gamma_{Pu^{3+}}}{\gamma_{Pu^{4+}}}}_{E^{o'}} - \frac{1}{nf}\ln\frac{C_{Pu^{3+}}}{C_{Pu^{4+}}} = E^{o'} - \frac{1}{nf}\ln\frac{KC_{Cl^-}^{x}C_{Pu^{3+}}}{C_{PuCl_x}} \qquad \text{Eq 3}$$

$$\begin{cases} k_{c,Pu^{3+}}\left(C_{Pu^{3+}}^{*} - C_{Pu^{3+}}\right) = \dfrac{i_a}{nFA} \Rightarrow C_{Pu^{3+}} = \dfrac{i_{a,lim} - i_a}{nFAk_{c,Pu^{3+}}} \\ -k_{c,PuCl_x}\left(C_{PuCl_x}^{*} - C_{PuCl_x}\right) = \dfrac{i_c}{nFA} \Rightarrow C_{PuCl_l} = \dfrac{i_{c,lim} - i_c}{-nFAk_{c,PuCl_x}} \end{cases} \qquad \text{Eq 4}$$

$$E = E^{o'} - \frac{1}{nf}\ln\left(KC_{Cl^-}^{*}\frac{\dfrac{i_{a,lim} - i_a}{nFAk_{c,Pu^{3+}}}}{\dfrac{i_{c,lim} - i_c}{-nFAk_{c,PuCl_x}}}\right) = \underbrace{E^{o'} - \frac{1}{nf}\ln K - \frac{1}{nf}\ln\frac{k_{c,PuCl_x}}{k_{c,Pu^{3+}}} - \frac{x}{nf}\ln C_{Cl^-}^{*}}_{E_{1/2}} - \frac{1}{nf}\ln\frac{i_a - i_{a,lim}}{i_{lim} - i} \qquad \text{Eq 5}$$

Where E, $\underline{E^{o'}}$, and $E_{1/2}$ are reduction potential, formal potential, and half-wave potential, respectively; n, the stoichiometric number of electrons involved in Eq 1, $n = 1$ for Eq 1; K, the equilibrium constant of the complexation reaction (Eq 2); C_j*, the bulk concentration of species j (j = M (metal), L (ligand), and ML (complex)); C_j, the concentration of species j at the electrode surface, $C_{Cl^-} \approx C_{Cl^-}{}^{*} \approx$ constant as $C_{Cl^-}{}^{*} >> C_{Pu}$*; $f \overset{\text{def}}{=} F/(RT)$, with F being the Faraday constant (96485 C/mol), R the ideal gas constant (8.314 J/mol·K), and T the temperature in Kelvin (T = 298.15 K in this case); A, the electrode surface area; $k_{c,j}$, the mass-transfer coefficient of species j; $i_{a\ or\ c,lim}$, anodic or cathodic limiting current, defined as the anodic or cathodic current $i_{a\ or\ c}$ when $C_j \ll C_j$*, namely $i_{a,lim} = -nFAk_{c,Pu^{3+}}C_{Pu^{3+}}^{*}$ and $i_{c,lim} = -nFAk_{c,PuCl_l}C_{PuCl_l}^{*}$. Hence, plotting $E_{½}$ against

the natural logarithm of the $Cl^{1-}_{(aq)}$ concentration enables the calculation of the number of Cl^{1-} ligands bound by plutonium.

III. References

1. W.H. Zachariasen, *Acta Crys*., **1948**, *1*, 268, DOI: 10.1107/S0365110X48000715.
2. C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler and P. A. Wood, *J. Appl. Cryst*., **2020**, *53*, 226-235. DOI: 10.1107/S1600576719014092.
3. Bard, A. J.; Faulkner, L. R.; White, H. S. Electrochemical Methods: Fundamentals and Applications; John Wiley & Sons, 2022.