Supplementary Material for:

Surprising formation of quasi-stable Tc(VI) in high ionic strength alkaline media.

Sayandev Chatterjee,* †[a] Gabriel B. Hall, †[a] Isaac E. Johnson,[a] Yingge Du,[b] Eric D. Walter,[b] Nancy M. Washton,[b] Tatiana G. Levitskaia*[a]

[a.] *Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, Washington 99354, United States; email:*
   Sayandev.Chatterjee@pnnl.gov, Tatiana.Levitskaia@pnnl.gov
[b.] *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99354, United States*
† *Authors contributed equally to the work*

Methods

Radiation safety disclaimer! *Technetium-99 has a half-life of 2.12 x10^5 years and emits a low-energy (0.292 MeV) β particle; common laboratory materials provide adequate shielding. Normal radiation safety procedures must be used at all times to prevent contamination.*

Chemicals and Materials. $KTcO_4$ and NH_4TcO_4 were in-house stocks available at the Radiochemical Processing Laboratory at Pacific Northwest National Laboratory, WA, USA. Potassium ferricyanide ($K_3[Fe(CN)_6]$) and potassium nitrate (KNO_3) were obtained from Sigma-Aldrich and used without further purification. Sodium hydroxide (NaOH) was obtained from Fischer Scientific.

Instrumentation and methods. Electrochemical measurements were carried out using a standard three-electrode cell with a Bioanalytical Systems (BASi) Epsilon Potentiostat. For cyclic voltammetry measurements, either a 3-mm glassy carbon or 1 mm platinum disk was used as a working electrode with a platinum wire being utilized as an auxiliary electrode. All reported potentials were referenced versus a 3.5 M Ag/AgCl reference-electrode. Due to dissolution of vycor frits under 1 and 2 M NaOH solutions, a Teflon fritted reference electrode commercially available from CH Instruments Inc. was used. Peak currents (i_p) were measured with respect to the extrapolated baseline current as described by Kissinger and Heineman.[1]

Spectroelectrochemical measurements were conducted in a BASi thin layer absorbance cell (1 mm pathlength) with a platinum 100 mesh electrode obtained from Sigma-Aldrich (99.9%, 2980931) as the working electrode. UV-vis absorption spectra were acquired using a deuterium light source (Mikropack, model# DH 2000) and a halogen light source (Mikropack, model# DH 2000), an Ocean Optics USB2000 detector (188-880 nm), and Spectra Suite software for spectral data recording.

The electrolytic generation of the reduced Tc species in oxidation states lower than Tc(VII) was determined by ^{99}Tc NMR and EPR spectroscopic techniques, which provide means for probing Tc in the odd diamagnetic and even paramagnetic oxidation states, respectively. ^{99}Tc NMR data were collected at 67.565 MHz on a 300 MHz Tecmag Discovery spectrometer equipped with a 10-mm broadband Nalorac probe.[2] The NMR solutions were placed in capped polyfluroroethylene/fluorinated ethylene-propylene copolymer sleeves (Wilmad), which were then inserted into 10 mm glass NMR tubes to provide secondary containment for the radioactive liquids.[2] A 5 mM TcO_4^- solution was used as a ^{99}Tc chemical shift reference and all chemical shift data are quoted relative to TcO_4^-.[3] EPR spectra were acquired on a Bruker EMX Spectrometer equipped with an ER4102ST resonator (spectra at room temperature and 120 K) or an ER4116DM Dual Mode resonator (spectra at 5 K) and an Oxford ESR910 cryostat. Samples were doubly contained by employing unbreakable FEP tube liners (Wilmad) inside traditional quartz EPR tubes. Sample solutions were placed into 1.5 mm inner diameter (ID) liners inserted into 4 mm outer diameter (OD) quartz tubes. To measure frozen solution and solid samples, 3.15 mm ID liners and 5 mm OD tubes were used. Hyperfine constants and g-values were extracted from the spectra via least squares fitting of the spectra with the EasySpin software package.[4]

X-Ray photoelectron spectroscopy (XPS) was used to confirm the Tc oxidation states associated with the species obtained from TcO_4^- electro-reduction. Spectra were recorded on a Kratos AXIS Ultra DLD system equipped with a monochromatic Al Kα x-ray source (1486.7 eV) at 10 mA, 15 kV for excitation and a hemispherical analyzer. Samples were mounted using double-sided Scotch brand tape attached to a silicon substrate. In order to obtain the photoelectron spectrum of the electro-reduced species in solution, a drop of isolated electrolyzed solution was placed on a carbon platform and allowed to evaporate under normal atmospheric conditions. The instrument work function was calibrated to give a binding energy of 83.96 ± 0.1 eV for the Au $4f_{7/2}$ line for metallic gold and the spectrometer dispersion was adjusted to give a binding energy of 932.62 ± 0.1 eV for the Cu $2p_{3/2}$ line of metallic copper. High-resolution analyses were carried out with an analysis area of 300 x 700 microns using pass energy of 40 eV with a step size of 0.1 eV. The samples experienced variable degrees of charging, and 1 eV bias electrons were used to minimize this charging. The surface charge was eliminated by charge neutralizer, and data were corrected relative to the reference 285.0 eV carbon 1s peak. The sample elemental composition was determined on the basis of the relative peak areas for each element and their corresponding sensitivity factors. XPS peak fitting was performed using CasaXPS software with Shirley type background and 20% Gussian-Lorentzian ratio.
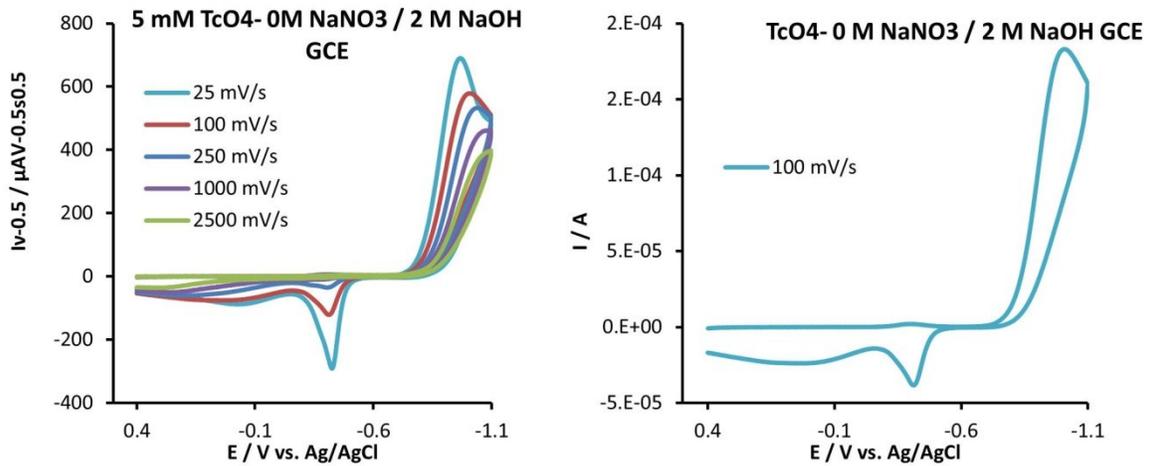
Figure S1. Cyclic Voltammetry of 5 mM TcO_4^- with no $NaNO_3$ present, and 2 M NaOH on a glassy carbon working electrode (GCE). Voltammograms are background subtracted.
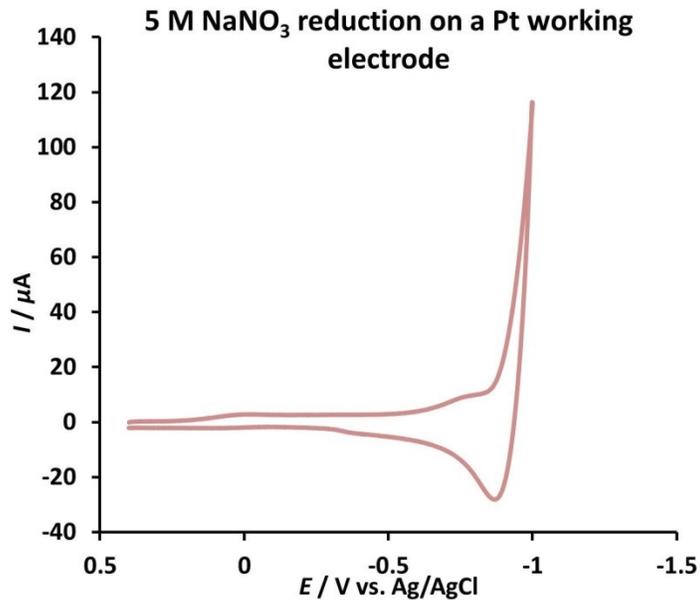
Figure S2. Direct reduction of 5 M $NaNO_3$ on a Pt disk working electrode.
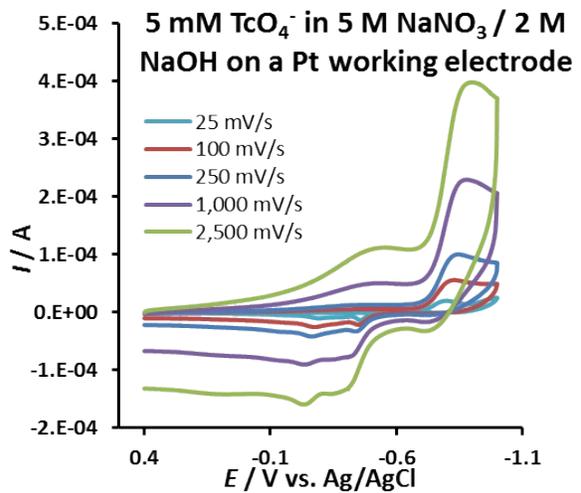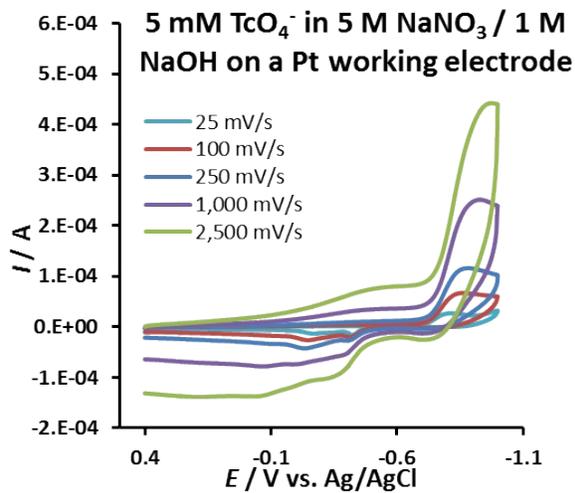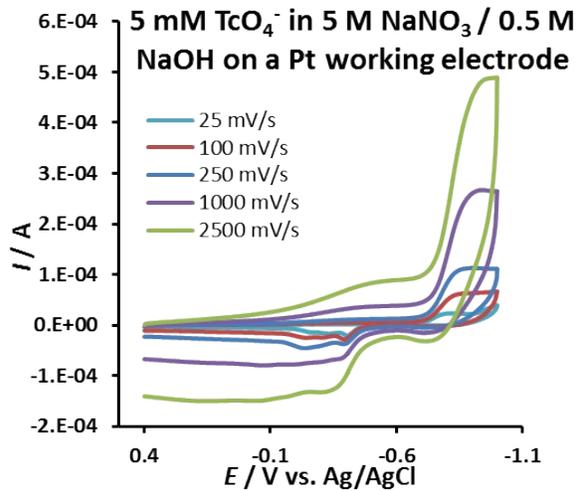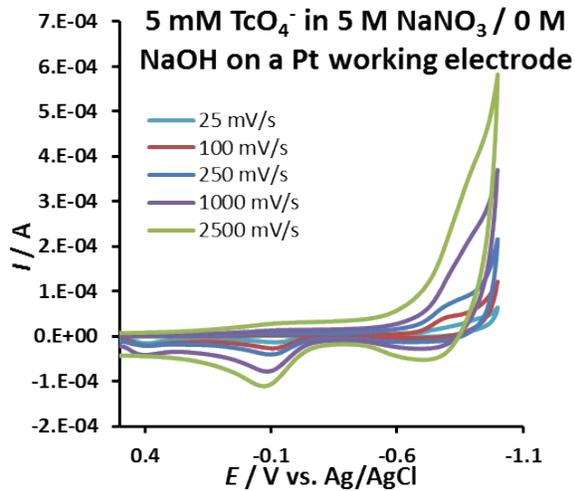
Figure S3. Cyclic voltammetry of 5 mM TcO_4^- in an aqueous solution containing 5 M $NaNO_3$ and various concentrations of NaOH. The voltammograms are not background subtracted.
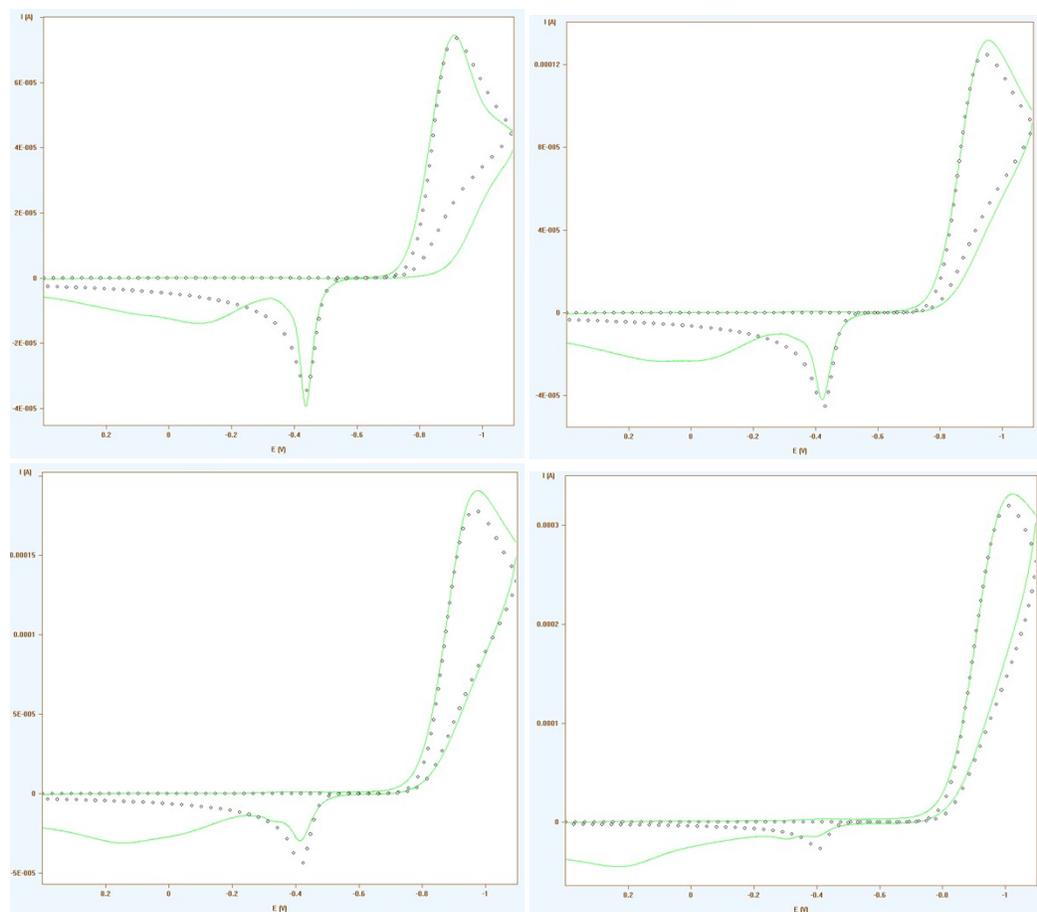
Figure S4. DigiElch modeling of voltammograms of 5 mM TcO_4^- in 5 M $NaNO_3$ / 2 M NaOH. Scan rates of 25 mV/s (top left), 100 mV/s (top right), 250 mV/s (bottom left), and 1,000 mV/s (bottom right). (dashed, grey lines) simulation, (solid, green line) experimental data. Mechanism and constants are given in Figure S5.

Define Mechanism and Strating Parameters

Chemical Reactions | Surface Reactions | Simulation Parameters

	Charge-Transfer Reaction	E° (V)	α ○ λ (eV)	ks (cm/s)
1	TcO4- + e = TcO4-2	-0.9091	0.35	0.0081351
2	TcO4- + 2e <= (TcO)O(OH)32-	-0.4372	0.3	0.008
3				
4				
5				

	Chemical Reaction	Keq	kf	kb
1	TcO4-2 + H2O= TcO3OH- + OH-	1E+007	1.8	1.8E-007
2	TcO3OH- + H2O= (TcO)O(OH)3-	1E+007	0.033762	3.3762E-009
3	(TcO)O(OH)3- + TcO4-2= (TcO)O(OH)32- + TcO4-	1E+008	20000	0.0002
4				
5				

	Species	Boundary	D (cm²/s)	Canal (mol/l)	Cinit (mol/l)
1	TcO4-	ORB	1.2432E-005	0.005054	0.005054
2	TcO4-2	ORB	1.2432E-005	0	0
3	H2O	ORB	2.1E-005	55	55
4	TcO3OH-	ORB	2E-005	0	0
5	OH-	ORB	2E-005	2	2

Ok   Cancel

Figure S5. Simulation parameters used in **Figure S4.**

References:

1   P. T. Kissinger and W. R. Heineman, *J. Chem. Educ.*, 1983, **60**, 702–706.

2   H. Cho, W. A. De Jong, B. K. McNamara, B. M. Rapko and I. E. Burgeson, *J. Am. Chem. Soc.*, 2004, **126**, 11583–11588.

3   K. J. Franklin, C. J. L. Lock, B. G. Sayer and G. J. Schrobilgen, *J. Am. Chem. Soc.*, 1982, **104**, 5303–5306.

4   S. Stoll and A. Schweiger, *J. Magn. Reson.*, 2006, **178**, 42–55.