Electrochemical and spectroelectrochemical investigations of TcO_4^- electroreduction in acidic media

Maciej Chotkowski, Andrzej Czerwiński

Faculty of Chemistry
University of Warsaw

7th International Symposium on Technetium and Rhenium – Science and Utilization, Moscow 4-8 July 2011

overview

- ✓ technetium and nuclear waste
- ✓ techniques
- ✓ influence of surface, H_2SO_4 and TcO_4^- concentration on the electroreduction of TcO_4^- ions
- ✓ influence of temperature on the electroreduction of TcO_4^- ions in H_2SO_4
- ✓ summary

technetium and nuclear waste

- TcO_4^-: high mobility in environment

$E^0_{TcO2/TcO4-}$ = 0.75V;

$E^0_{TcO(OH)2/TcO4-}$ = 0.58V

$E^0_{H2O/O2}$ = 1.23V

$TcO_2*1{,}6H_2O \leftrightarrow TcO(OH)_2 + 0.6H_2O$ $\quad K = 10^{29,4}$

$TcO^{2+} + H_2O \leftrightarrow TcO(OH)^+ + H^+$ $\quad K = 10^{-1,37}$ (0,1M KNO_3)

$TcO(OH)^+ + H_2O \leftrightarrow TcO(OH)_2 + H^+$ $\quad K = 10^{-2,43}$ (0,1M KNO_3)

$TcO(OH)_2 + H_2O \leftrightarrow TcO(OH)_3^- + H^+$ $\quad K = 10^{-10,89}$ (0,1M KNO_3)

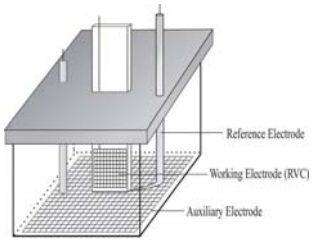
$TcO_4^- \rightarrow Tc(VI,V)(disprop./electrored.) \rightarrow TcO_4^- + Tc(IV) \rightarrow Tc(III)$

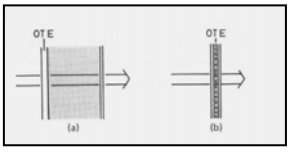
techniques

- cyclic voltammetry (CV), chronoamperometry (CA)
- rotating ring disc electrode (Au-RRDE)
- spectroelectrochemistry

  - optically transparent electrodes (Au-OTE)

  - optically transparent thin layer electrodes (RVC-OTTLE)

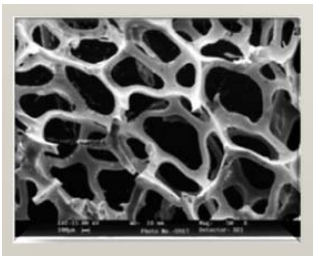




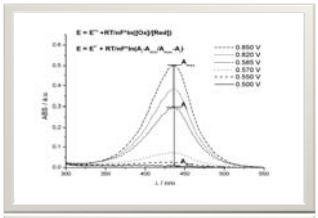
Reticulated Vitreous Carbon (RVC®)

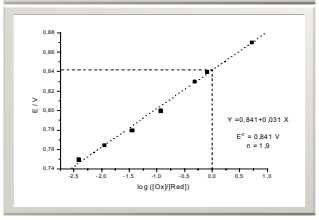
application as an electrode material

Physical properties	Values	
	RVC	GC
Density [kg m^{-3}]	48	1650
Void volume [%]	90 - 97%	0
Bulk resistivity [Ω cm]	0.005	0.001
Thermal cunductivity [cal cm ^{0}C w 10^{-4} tor]	0.08-1200	0.01 – 0.02

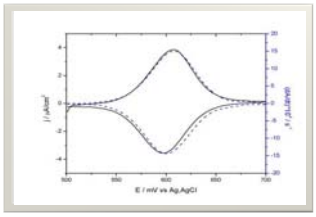


spectroelectrochemistry UV-Vis





Spectroscopic signals recorded during chronoamperometric oxidation of 0.4 mM o-tolidine0.5 M CH_3COOH + 0.1 $HClO_4$



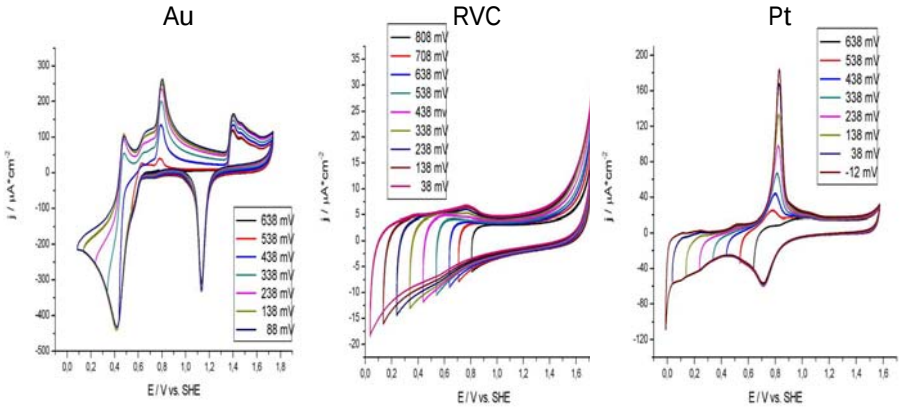
Cyclic voltammogram and voltabsorbommogram 0.4 mM o-tolidine + 0.5 M CH_3COOH + 0.1 $HClO_4$ v = 0.2 mVs^{-1}, λ = 438 nm

$$j = nFc\left(D\nu\frac{nF}{RT}\right)^{1/2} f(w,\xi)$$

$$\left(\frac{dA}{dt}\right) = \in c\left(D\nu\frac{nF}{RT}\right)^{1/2} f(w,\xi)$$

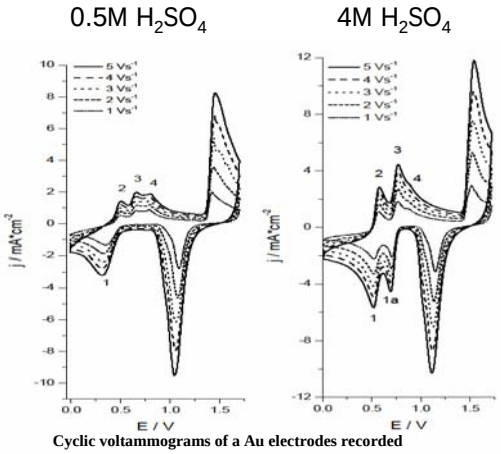
S. Zamponi, A. Czerwinski, R. Marassi
J. Electroanal. Chem. 266 (1989) 37

influence of surface on the electroreduction of TcO_4^- ions



Cyclic voltammograms of a Au, RVC and Pt electrodes recorded for various cathodic vertex potentials in 1 mM $KTcO_4$ + 0.5M H_2SO_4, v = 50 mV s^{-1}.

influence of H_2SO_4 concentration on the electroreduction of TcO_4^- ions



Cyclic voltammograms of a Au electrodes recorded for various scan rates in $KTcO_4$ + H_2SO_4.

Electroreduction:

peak 1a Tc(VI) and Tc(V)

Peak 1 Tc(IV) and Tc(III)

Electrooxidation:

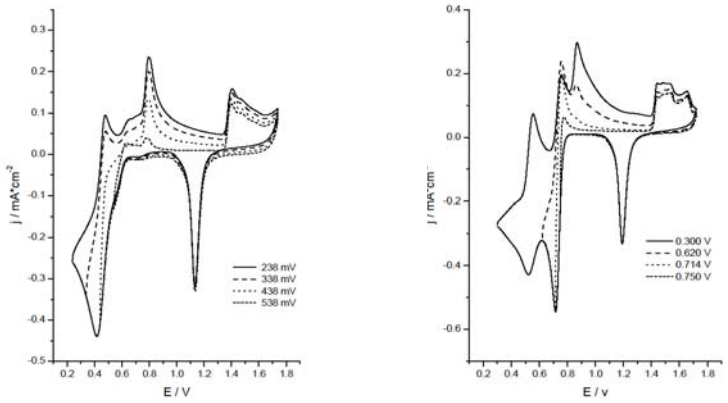
peak 2 Tc(IV)

peak 3 Tc(VI)

peak 4 Tc(VII)

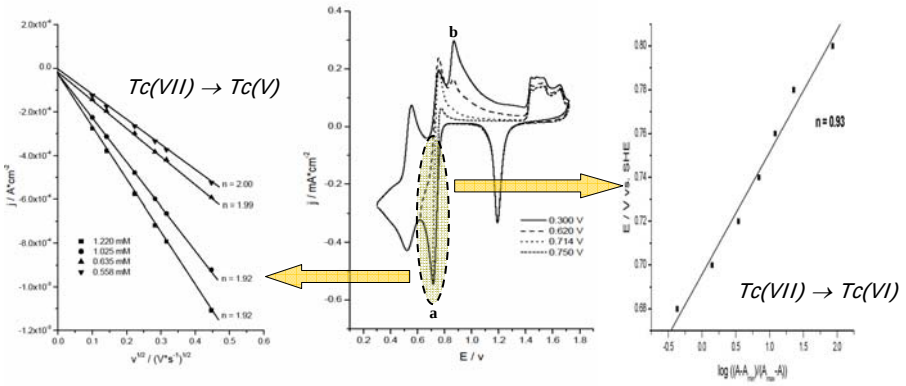
influence of H_2SO_4 concentration on the electroreduction of TcO_4^- ions

0.5M H_2SO_4 | 4M H_2SO_4



Cyclic voltammograms of a Au electrodes recorded for various cathodic vertex potentials in $KTcO_4 + H_2SO_4$, v = 0.05Vs^{-1}

influence of TcO_4^- ions concentration on the electroreduction in 4M H_2SO_4

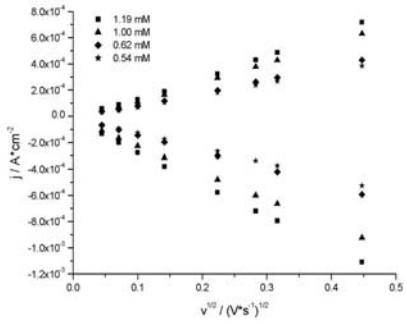


Peak current density as a function of square root of the scan rate recorded in 4M H_2SO_4 for different concentration of $KTcO_4$.

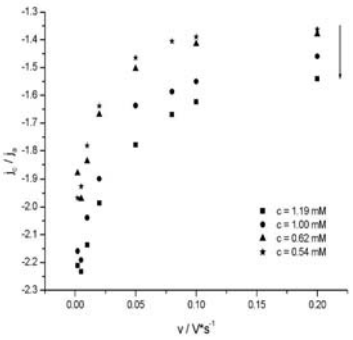
Cyclic voltammograms recorded in 4M H_2SO_4 + 1,19 mM $KTcO_4$ for different cathodic vertex potentials, v = 0.05 Vs^{-1}.

E vs. log ([Ox]/[Red]) plot. Spectroelectrochemical experiments recorded in 4M H_2SO_4 + 1,19 mM $KTcO_4$ Au-OTE

influence of TcO_4^- concentration on the electroreduction process

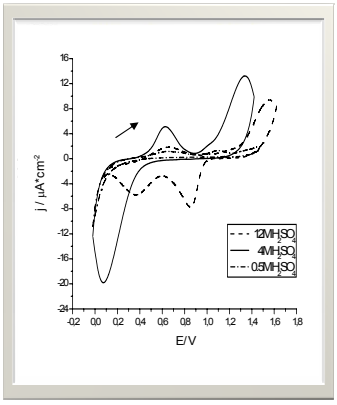


Peaks a and b currents as a functions of $v^{1/2}$ recorded in 4M H_2SO_4 for various concentrations of TcO_4^-, Au electrode,



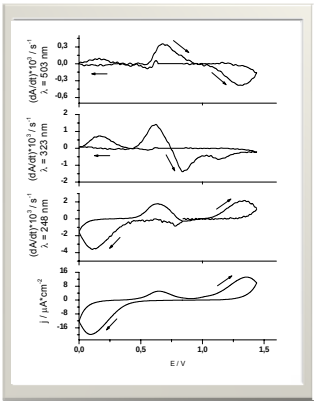
j_c/j_a vs scan rate recorded in 4M H_2SO_4 for various concentrations of TcO_4^-, Au electrode,

influence of H_2SO_4 concentration on the electroreduction of TcO_4^- ions



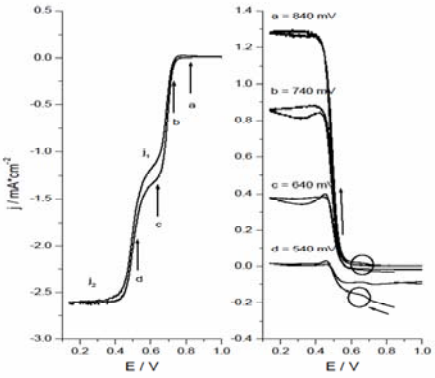
Cyclic voltammograms of a RVC-OTTLE electrodes recorded for various concentrations of H_2SO_4,

1mM $KTcO_4$, v = 0.2 mVs^{-1}

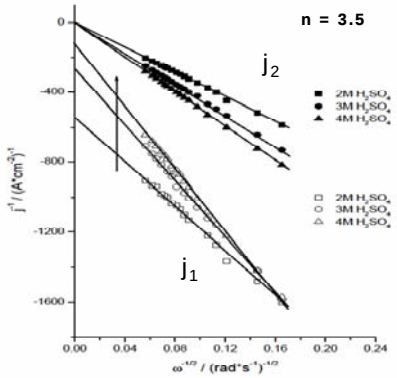


Cyclic voltammogram and voltabsorbommograms recorded and calculated for RVC-OTTL electrode in 1 mM $KTcO_4$ + 4M H_2SO_4 v = 0.2 mVs^{-1}

influence of H_2SO_4 concentration on the electroreduction of TcO_4^- ions



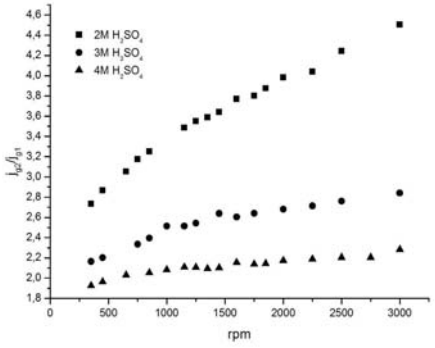
Left panel: cyclic voltammogram of a gold disc electrode of a RRDE assembly with rotation speed of 1600 rpm in 0.55mM $KTcO_4$ + 4M H_2SO_4, v = 2Vmin^{-1}. Right panel: ring electrode currents measured simultaneously to CV shown on the left panel for various constant potentials of the ring and indicated on the plot.



Reverse Levich plots for the limiting current of pertechnetate reduction current recorded at a gold electrode in various H_2SO_4 solutions, v = 2Vmin^{-1}.

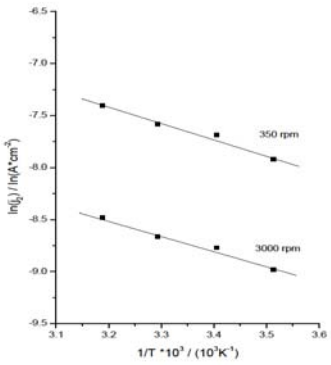
M.Chotkowski, A.Czerwiński, Electrochemical and spectroelectrochemical investigations of TcO_4^- electroreduction in acidic media

influence of H_2SO_4 concentration on the electroreduction of TcO_4^- ions

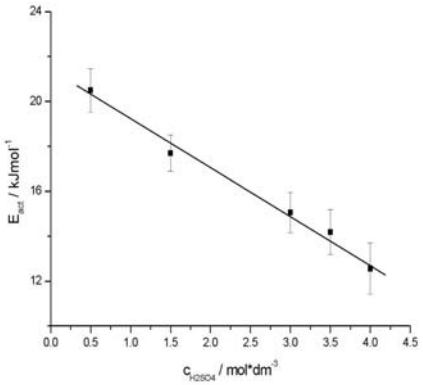


Reverse Levich plots for the limiting current of pertechnetate reduction current recorded at a gold electrode in various H_2SO_4 solutions, v = 2Vmin^{-1}.

influence of temperature, H_2SO_4 concentration on the electroreduction of TcO_4^- ions

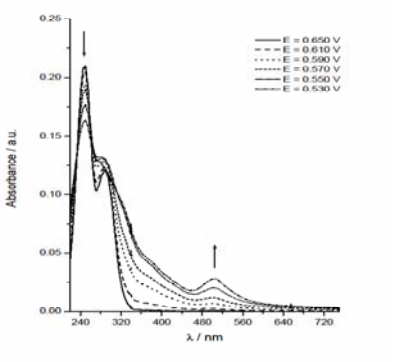


***lnj* vs. T^{-1} plot for j_2 limiting current of pertechnetates reduction current recorded on a gold electrode in $4H_2SO_4$ + 0.32 mM $KTcO_4$**

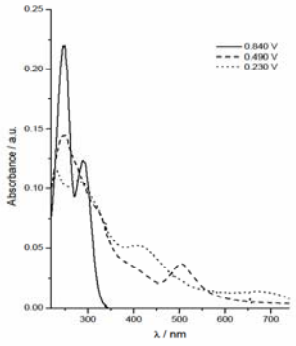


Calculated activation energy for j_2 as a function of H_2SO_4 concentration in H_2SO_4 + 0.32 mM $KTcO_4$

spectroelectrochemistry of technetium in 4M H_2SO_4



UV-Vis spectra recorded during chronoamperometric reduction of pertechnetates in 4M H_2SO_4 + 1.19mM $KTcO_4$, potential range 0.65V+0.53V, Au-OTE



UV-Vis spectra of TcO_4^- (E= 0.84V), polymeric Tc(IV) (E = 0.49V) and Tc(III) (E = 0.23V) recorded in 4M H_2SO_4 + 1.19mM $KTcO_4$ Au-OTE

summary

- ✓ Concentration of the sulfuric acid has a significant influence in the electrochemical reduction of pertechnate ions.
- ✓ Tc species on lower oxidation states and generated during reduction of pertechnates are stabilized at higher concentrations of H_2SO_4.
- ✓ The peak related to electroreduction of pertechnetates to Tc(VI,V) is much better developed in 4M H_2SO_4 as compared to 0.5M solution,
- ✓ In the first step of discussed Tc(VII) reduction process the TcO_4^- ions are reduced on the surface of Au electrode to technetium(VI) and later to Tc(V).
- ✓ Tc(V) can disproportionate to Tc(IV) and Tc(VI).

M.Chotkowski, A.Czerwiński, Electrochemical and spectroelectrochemical investigations of TcO_4^- electroreduction in acidic media

summary

- ✓ In hydrodynamic experiments the soluble, polymeric technetium(III,IV) species are generated. These species are formed during the process with rate controlled by diffusion as follows from the low value of activation energy.
- ✓ The polymeric species can be also detected spectroscopically by a band at 502 nm.
- ✓ Polymeric technetium species can be reduced to Tc(III) which can be spectroscopically characterized by a band at 670 nm.

Thank You

19