Study on the determination of trace rhenium (VII) by the adsorption differential pulse polarography

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Abstract The determination of trace rhenium (VII) by differential pulse polarography in the system of H_2SO_4-$(NH_2OH)_2 \cdot H_2SO_4$-TeO_4^{2-} is markedly improved by the addition of Nitron, which is adsorbed on the surface of mercury electrode. The limit of detection is down to 2×10^{-10} M. The adsorptive peak potential is -0.80 V (vs. SCE). In the ranges of 5×10^{-10}—10^{-8}, 1×10^{-8}—10^{-7} and 1×10^{-7}—10^{-6}M, there are good linear relationships between the peak current increment and the concentration, of which the relative standard deviations are 9.5, 6.6, 1.8% respectively with the correlation coefficients of linear regression of 0.995—0.999. The results relating to this polarographic wave show that it is an adsorption-catalytic wave. The mechanism of the electrode reaction is discussed.

Györbiro firstly showed that TeO_4^{2-} can produce a catalytic wave in the presence of ReO_4^-, by which trace amount of rhenium in molybdenite was determined.[1] But the sensitivity did not meet the practical requirement. Later on, based on the catalytic system, a series of efforts had been made by some authors.[2-5] Thus, the limit of determination of Re was about 5.4×10^{-9} M.

In this paper the base electrolyte is further improved by adding Nitron which reacts with ReO_4^- to form a precipitate, which is adsorbed on the surface of mercury electrode. By using suitable amount of ethanol to suppress the blank peak from TeO_4^{2-} and to reduce the solubility of the precipitate, and by optimizing the experimental conditions, the concentration of ReO_4^- as low as 2×10^{-10} M can be detected. In the range of 5×10^{-10}—10^{-8}, 1×10^{-8}—10^{-7} and 1×10^{-7}—10^{-6} M ReO_4^-, the relationship between peak current increment and concentration is in good linearity.

From the electrocapillary curves, $i_p \sim H(\mathrm{Hg})$, $i_p \sim \tau$, $i_p \sim t(℃)$, and the curves of cyclic voltammetry, the polarographic wave is proposed to be an adsorption-catalytic wave. Furthermore, the mechanism of the electrode reaction is discussed.

Experimental

Instruments

Metrohm Polarecord E506, VA controller E608, Multi-Dosimat 655, Metrohm 663 VA

Received May 18, 1987.

stand and E505 stand (Metrohm Herisau, Switzerland). SDME, HDME are working electrodes, SCE reference electrode, Pt counter electrode, Metrohm cell with constant thermostat.

JW–0.001°C Type thermostat, MF–A Multiple function Voltammetry Instruments (Analytical Instrument Factory, Jiangsu), 3086 Type X–Y Recorder (Yokogawa Hokushin, Tokyo).

Reagents

1.00×10^{-3} M ReO_4^- stock solution from NH_4ReO_4 (99.99%). 50 ppm Te(VI) TeO_4^{2-} standard stock solution prepared according to the literature.[2] 5% Nitron: 0.5g Nitron ($C_{20}H_{16}N_4$) is dissolved in a suitable amount of water and 0.5 mL glacial acetic acid, then diluted to 10 mL with water in a measuring flask and protected from light.

All reagents except hydroxyamine sulphate (C. P.) are of analytical grade.

Twice–quartz–distilled water by sub–boiling distiller is used throughout the whole process.

Procedure

Add a definite volume of ReO_4^- solution to be measured to 25.00 mL solution which consists of 3.2 M H_2SO_4, 3.1×10^{-7} M TeO_4^{2-}, 1.8% Na_2SO_4, 0.8% $(NH_2OH)_2 \cdot H_2SO_4$, 10% ethanol and 160 ppm Nitron. An aliquat of the test solution was put into the electrolyte cell to record differential pulse polarograms in the range of potential of −0.4V — −0.9V (vs. SCE).

Due to the overlap of the new peak produced by ReO_4^- on that of TeO_4^{2-} (as background-peak), the increment of polarographic peak is measured for the determination of Re (VII), and is also described as i_p. The differential pulse polarograms of TeO_4^{2-} and ReO_4^- are given in Fig. 1.

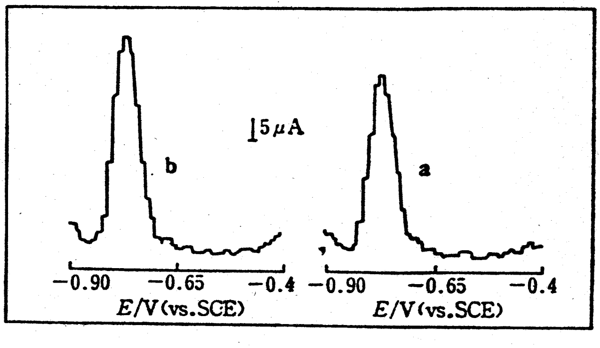

Fig. 1 The differential pulse polarograms of TeO_4^{2-} and ReO_4^-
a) Base electrolyte + 3.1×10^{-7} M TeO_4^{2-}, $E_p = -0.80$ V.
b) (a) + 2.00×10^{-9} M ReO_4^-, $E_p = -0.80$ V.

Results and discussions

The choice of experimental conditions

(1) The influence of the amount of H_2SO_4

The increment brought by ReO_4^- (2×10^{-8} M) would obviously varies with the concentration of H_2SO_4. In neutral solution no TeO_4^{2-} peak appears near -0.80 V. Thus, there is no increment produced by ReO_4^-. With the increasing of H_2SO_4 concentration, at first the height of the polarographic peak rises, then falls down. In the range of 2.5—3.6 M H_2SO_4, the change of peak height is slow. It is shown that 3.2 M is the suitable concentration of H_2SO_4.

(2) The choice of the amount of Te (VI)

The experimental results show that the sensitivity for determining ReO_4^- depends upon the amount of TeO_4^{2-} used. When TeO_4^{2-} is too little, it is not sensitive. When TeO_4^{2-} is too much the sensitivity is reduced because the value of the blank peak greatly increases. In the range of 1×10^{-9}—5×10^{-7} M of ReO_4^- the experimental results show that 3.1×10^{-7} M TeO_4^{2-} is suitable.

(3) The effect of Nitron on the peak current

The effect of Nitron on the peak current is shown in Fig. 2. Suitable amount of Nitron can increase the sensitivity for determining ReO_4^- by one order of magnitude.

In this work the concentration of 160 ppm was chosen for Nitron.

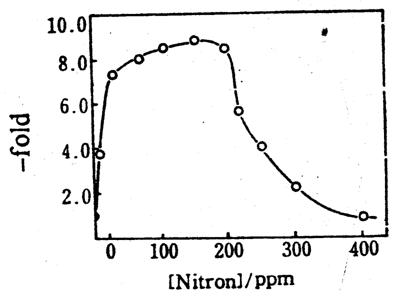

Fig. 2 The effect of Nitron on the sensitivity for the determination of trace Re (VII)
$[ReO_4^-]=2.00 \times 10^{-8}$M
$[TeO_4^{2-}]=3.1 \times 10^{-7}$M

(4) The influence of the concentration of $(NH_2OH)_2 \cdot H_2SO_4$ and Na_2SO_4

It was found that a small amount of hydroxyamine sulfate can improve the slope of the polarographic wave and raise slightly the height of the current peak. Excess hydroxyamine sulphate would reduce the sensitivity because it gives a new peak. The addition of Na_2SO_4 does not considerably influence the height of the peak, but can improve the shape of the polarographic wave and eliminate the peak of $(NH_2OH)_2 \cdot H_2SO_4$. Experimental results showed that 0.8% $(NH_2OH)_2 \cdot H_2SO_4$ and 1.8% Na_2SO_4 are suitable for the purpose.

(5) The influence of ethanol

The addition of ethanol can improve the shape of the polarographic wave and reduce the background current. Suitable amount of ethanol can raise the sensitivity for about 2 fold. Here, 10% (v/v) ethanol was chosen.

Although the choice of the amount of every component was studied separately, experimental results showed that any slight deviation from the chosen value of one component does not change the optimum values much. Therefore, 3.2 M H_2SO_4, 3.1×10^{-7} M TeO_4^{2-}, 160 ppm Nitron, 0.8% $(NH_2OH)_2 \cdot H_2SO_4$, 1.8% Na_2SO_4 and 10% (v/v) ethanol are chosen as the base electrolyte.

The relationship between the increment of the peak height and Re (VII) concentration

In the ranges of 5×10^{-10}—10^{-8}, 10^{-8}—10^{-7}, and 10^{-7}—10^{-6} M, linear regression results showed that the peak increment is proportional to the concentration of ReO_4^-. The slopes are 2.85×10^9, 3.07×10^9 and 3.12×10^9 (nA/M) respectively with the correlation coefficients of 0.995—0.999.

Interference test

Under the above selected optimum conditions for the supporting electrolyte system, foreign ions were added to the solution. It was shown that ions of Zn^{2+}, Mn^{2+}, Ga(III), Co^{2+}, Ni^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and $H_2BO_3^-$ up to millionfold of the concentration of ReO_4^- can be present without interfering. The results of interfering ions are shown in Table 1.

Table 1 Interfering test

Interference ions	ratio of $[Ion]/[ReO_4^-]$ Interference observable	20% interference	Interference observed	Change of wave shape
Fe^{3+}	20	2440	+	little
In^{3+}	2236	3956	+	no
Sb(III)	1200	2000	−	worse
Bi(III)	1000	2240	−	no
Cu^{2+}	10	2220	−	worse
Pb^{2+}	30	250	+	no
Cd^{2+}	120	300	+	no
Tl^+	10000	20000	+	high conc. worse
Ag^+	114	7640	−	no
MoO_4^{2-}	10	600	+	no
WO_4^{2-}	800	6440	−	worse
CrO_4^{2-}	100	430	−	no
VO_3^{2}	250	1300	+	no
AsO_2^-	1440	1940	−	worse

"+" positive errors, "−" negative errors. $[ReO_4^-] = 2.00 \times 10^{-8}$M.

However, most of the interfering ions can be removed by the addition of $Ca(OH)_2$, and the introduction of CO_2.[2] Since the precipitates of carbonates produced could be co-precipitated with $CaCO_3$, the solubility of $CaWO_4$, $CaCrO_4$, $CaMoO_4$ and the hydroxides of heavy metal ions is very small, whereas that of $Ca(ReO_4)_2$ is relatively large.

Experiments proved such separation to be effective.

It should be pointed out that it is necessary to examine the stability of the base solution in view of the possible chemical reaction between Hg and TeO_4^{2-}. Experiments show that in the absence of Hg, the peak height remains constant after many hours, which means that the base solution is stable. When the base solution is allowed to stand with large amount of mercury for a long time, both the blank peak and the catalytic peak are reduced about 1/5. However, in short time and with a little amount of mercury, this effect can be neglected.

Analysis of ore samples

1 mL sample solution which was prepared from ore sample (molybdenite) according to the literature[2] and 19 mL base solution whose concentration is 5% higher than that recommended above were put into the polarographic cell and bubbled with pure nitrogen for 10 minutes. At the range of —0.4 V to —0.9 V the polarograms were recorded. The amount of Re (VII) was determined by both calibration curve and standard addition method. The results were given in Table 2.

Table 2 Analysis of ore samples (in ppm)

Sample No.	1		2		3	
Measuring method	a*	b[5]	a*	b[5]	a*	b[5]
Standard addition	158	150	92.8	91.6	12.8	14.6
Calibration curve	156	152	90.1	89.1	12.3	13.2
average	157	151	91.5	89.9	12.6	13.9

* this method.

Mechanism of the electrode reaction

(1) The dependence of DPP peak current on the mercury height

The currents obtained from differential pulse polarography are different from those obtained from square wave polarography. They possess some DC polarographic properties.[6] The approximate equation of the peak current of DPP can be directly derived from that of DC polarographic wave.[7] It is similar to the DC polarography in that the peak current of DPP is proportional to the height of mercury, *i. e.*, the formula of $i_p = KH$ can also provide diagnostic criteria for the adsorbability in the electrode processes. Our experiments have proved that when Cd^{2+} is in the solution of 0.1 M KI, there is a linear relation between the peak current obtained and the mercury height, *i. e.*, $i_p = KH$. However, when Cd^{2+} is in the solution of 0.1 M KNO_3, $i_p \neq KH$. It has been found that adsorption takes place for Cd^{2+} in the solution of 0.1 M KI, but not in the solution of 0.1 M KNO_3. In Fig. 3, the curve (a) obtained from the known adsorption system of Cd^{2+} in 0.1 M KI was compared with (b) obtained from this system. Thus, it suggests that the current here possesses the adsorptive feature.

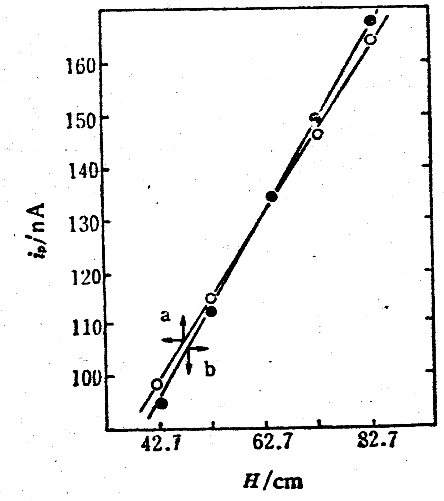

Fig. 3 Dependence of DPP peak current on the height of Hg

(2) Electrocapillary curves

Fig. 4 reveals the fact that the reagent Nitron is obviously adsorbed on the surface of mercury electrode at the range of potential of —0.2 V to —1.0 V (vs. SCE).

(3) The dependence of i_p on the rest time of HDME

It was shown that within 15 min at the potential of —0.6 V, the longer the rest time is, the higher i_p is. The peak current increases almost in linearity with rest time in this interval. Over 15 min, the current does not increase any more. This phenomenon is obviously an evidence that the electroactive reactants were adsorbed on the surface of HDME.

(4) The effect of temperature on peak current

In the range of 5 — 50°C, the effect of temperature on peak current is shown in Fig. 5. The curve of i_p vs t(°C) predicts a competition between the kinetic (catalytic) and adsorp-

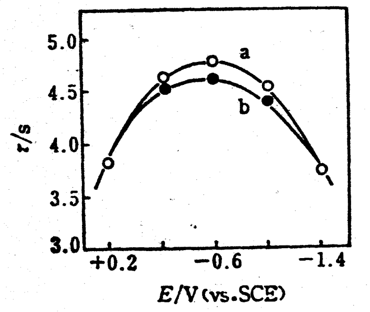

Fig. 4 Electrocapillary curves
a) Blank (without Nitron, but with TeO_4^{2-} and ReO_4^-).
b) With Nitron (with TeO_4^{2-} and ReO_4^-, or without TeO_4^{2-} and ReO_4^-).

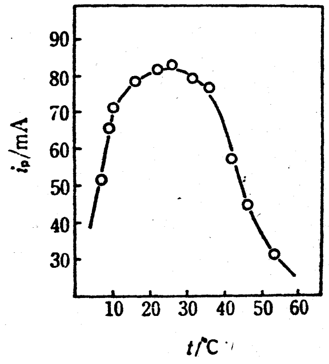

Fig. 5 i_p vs. t
The same test solution as that in Fig. 2.

tion processes in this system. Below 25°C adsorption is dominant, and the current is mainly controlled kinetically. The reaction rate and also the diffusion rate increased with the rising temperature, so the current increases with temperature. But at higher temperatures (>25°C), the kinetic reaction is fast enough for the current to be controlled by the amount of adsorption. Obviously, the amounts of electroactives adsorbed decrease with the rising temperature, thus the current reduces. In this system, the suitable temperature should be about 25°C for the determination of ReO_4^-.

(5) Cyclic voltammetric curves at HDME

The cyclic voltammograms obtained from solutions of different composition are shown in Fig. 6 (a, b, c, d). Curve (a) shows that Nitron does not evidently influence the cyclic voltammogram. The principal distinction between the curves (b), (c) and (d) lies in the change of peak current $(i_p)_3$ which is at the potential of -0.80 V. Though the peak current $(i_p)_3$ increases with the addition of ReO_4^- and Nitron, its shape and the other peaks, including $(i_p)_1$ and $(i_p)_2$ remain almost unchanged. These facts mean that the presence of both ReO_4^- and Nitron does not lead to any new electron transfer reaction at the surface of mercury electrode except the increase of $(i_p)_3$.

The anodic peak corresponding to cathodic peak $(i_p)_3$ was not found, which means that this step is irreversible.

As shown in Fig. 6 (b), it has been observed that the appearance of both $(i_p)_2$ and $(i_p)_3$ is due to the presence of TeO_4^{2-} as compared with Fig. 6 (a), and there are two reduction steps for Te (VI) at the electrode surface in this range of potential. The second reduction (corresponding to $(i_p)_3$) of Te (VI) is catalyzed by rhenium (VIII), and enhanced by Nitron (Fig. 6 (c)).

It is noteworthy that Nitron enhances $(i_p)_3$ only in the presence of ReO_4^-, and both TeO_4^{2-} and TeO_3^{2-} have the same polarographic peaks at identical potential.

As shown from the electrocapillary curve, Nitron will be adsorbed on the surface of

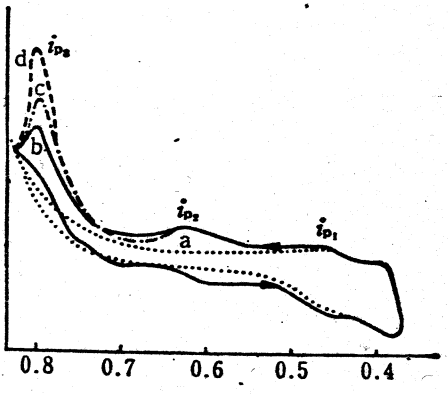

Fig. 6 Cyclic voltammograms

a) without TeO_4^{2-} and ReO_4^- in the solution, with or without Nitron;
b) containing TeO_4^{2-} only;
c) (b) $+2.00 \times 10^{-8}M$ ReO_4^-;
d) (c) +150 ppm Nitron.

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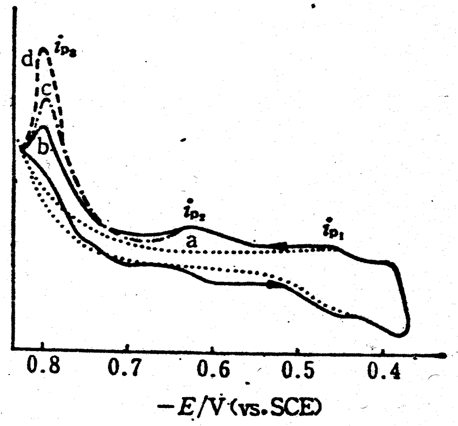

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b) containing TeO_4^{2-} only;
c) (b) $+2.00 \times 10^{-8}$M ReO_4^-;
d) (c) +150 ppm Nitron.

Hg electrode. Thus, Nitron may induce ReO_4^- to be adsorbed on it due to the formation of the precipitate of Nitron with ReO_4^-. According to the literature,[8-10] in acid solution ReO_4^- would be reduced at relatively more positive potentials to form ReO_2, which also get adsorbed on the surface of Hg electrode. Therefore, it may be ReO_2 which regenerates the reduction product of Te (the corresponding reduction peak current is $(i_p)_3$). In view of the fact that both TeO_4^{2-} and TeO_3^{2-} have identical polarographic peaks, both $(i_p)_2$ and $(i_p)_3$ must have resulted from the reduced product of Te (IV), not Te (VI).

(6) Normal pulse polarogram

A current peak appears in the normal pulse polarogram of the TeO_4^{2-} system containing ReO_4^-. It means that the reactant is adsorbed on the electrode surface. As mentioned above, in the absence of Nitron ReO_4^- is not adsorbed on the surface of Hg electrode,[8,11] and also at such a negative potential ReO_4^- has been reduced to ReO_2 or other products with lower valence. In view of these experimental results and the adsorption properties of ReO_2, we believe that ReO_2 is just the reactant which is adsorbed on the surface of Hg electrode and participates in the electrode reaction to yield the peak current (Fig. 7). From the peak potential and the current magnitude, these peaks in Fig. 7 correspond to $(i_p)_3$ in Fig. 6 (c).

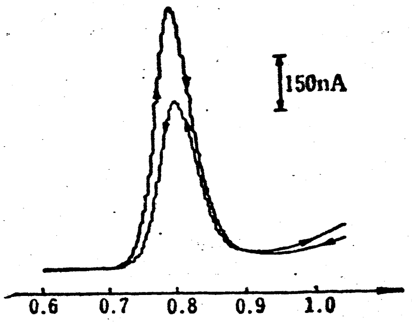


Fig. 7 Normal pulse polarogram for the system of ReO_4^--TeO_4^{2-}

During the period of reversal sweep, the decrease of the peak current suggests that the electrode reaction has relatively poor reversibility.

(7) The DC polarographic behaviour

With both the rapid and normal mode the DC polarograms exhibit current peaks. The current peak is not the maximum because of the presence of electroactive substances.

In order to reveal the mechanism of the catalytic reaction experiments were carried out to find the dependence of i_1 on m and τ under different heights of mercury. In order to clarify both adsorptive and catalytic effect, experiments were also carried out at both low temperatures and high temperatures. The results are given in Table 3.

At low temperature (7°C), $i_1 \propto \tau^{0.4}$: but at rather high temperature (25°C), $i_1 \propto \tau^{-0.16}$. This shows that the electrode reaction is controlled by both kinetic (catalytic) and adsorptive processes. Because of the predominance of adsorption at low temperature, the current is mainly controlled by the rate of catalytic reaction, so the index of τ tends to be 2/3. But at high temperature (25°C), the reaction is accelerated, and the adsorption effect is dominating.

Table 3 The dependence of DC polarographic current (i_1) on the drop time (τ)

Height of Hg (cm)	25°C				7°C			
	τ (s)	m (mg/s)	i_1 (nA)	$i'_1/\tau^{-0.16}$	τ (s)	m (mg/s)	i_1 (nA)	$i'_1/\tau^{0.4}$
34.5	4.71	1.40	15.68	16.06	4.77	1.42	9.1	3.86
44.5	3.63	1.84	20.07	16.43	3.71	1.84	9.9	3.91
54.5	2.94	2.24	23.52	16.32	3.02	2.25	10.05	3.77
64.5	2.49	2.67	27.23	16.37	2.54	2.67	10.40	3.73
74.5	2.15	3.10	30.30	16.11	2.38	2.86	10.75	3.77
84.5	1.88	3.51	33.66	16.13	1.97	3.45	11.75	3.92

$i'_1 = i_1/m^{2/3}$, $[ReO_4^-] = 1.00 \times 10^{-7}M$

Therefore the index of τ tends to be $-1/3$. When the temperature rises continuously till the adsorption mechanism no longer exists, the current falls down rapidly.

From the dependence of i_1 (DC) on m and τ it is obvious that the electrode processes are controlld by many factors. The results are in agreement with those mentioned above.

Conclusion

1) The whole electrode process is simultaneously controlled by both adsorption and kinetic (catalytic) step.

2) TeO_4^{2-} and TeO_3^{2-} produce an identical polarographic peak (blank peak) which comes from their reduction to the same low-valence substance.

3) The increase of peak current, which is used for determining trace rhenium (VII), is due to the catalytic reaction, in which the identical low-valence reduction product (Te^{2-}) yielded from either TeO_4^{2-} or TeO_3^{2-} is regenerated by ReO_2 resulted from the reduction of ReO_4^- to be determined.

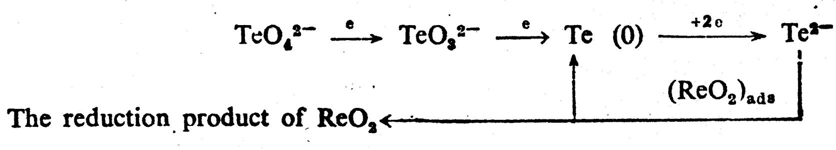
4) Due to the induced adsorption of ReO_4^- caused by the formation of the insoluble substance of Nitron with ReO_4^-, the catalytic reaction is greatly sensitized by Nitron.

5) According to the following reaction[12] (in the peak potential range of −0.78 V to −0.80 V (vs. SCE)), and also in view of the fact that in acid media ReO_4^- can be reduced at more positive potential to ReO_2 which is adsorbed on the Hg electrode surface, [9,10,13] the reactions involved may be postulated as follows:

$$Y + Hg \longrightarrow Y_{ads}\ (Hg) \quad \text{(Y stands for Nitron)}$$

$$Y_{ads} + ReO_4^- \longrightarrow [YReO_4^-]_{ads}$$

$$[YReO_4^-]_{ads} + 3e \xrightarrow{H^+} Y_{ads} + (ReO_2)_{ads}$$



Acknowledgement This project was supported by the National Natural Science Foundation of China. This work was also supported by the "Stiftung Volkswagenwerk Bundesrepublik Deutschland".

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