



Direct Experimental Support for the Catalytic Effect of Iron-Group Metals on Electrodeposition of Rhenium

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Previously, we reported an increase in the rate of deposition of Re when ions of Ni, Fe, or Co were added to the plating bath. The mechanism proposed was that the divalent ions were reduced to the metallic form, and the resulting atoms reduced the ReO_4^- ion chemically to Re^0 . Here, the validity of this mechanism was tested and found applicable by studying the chemical reduction at open circuit of ReO_4^- by iron-group metal foils or thin films. The coatings formed were studied by X-ray photoelectron spectroscopy, and the reduction of the ReO_4^- ion was proven.

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The electroplating of rhenium (Re) and its alloys with the iron-group metals (Me = Ni, Co, Fe) has been studied in our laboratory¹⁻³ in an effort to understand the mechanism and to develop suitable plating baths for the electrodeposition of Re and its alloys. The main results obtained in our previous articles can be summarized as follows:

1. Re can be electroplated from aqueous solutions containing an excess of citric acid, but the quality of the plated film is poor and the faradaic efficiency (FE) is low.

2. Adding any of the three cations of the iron group increases the rate of deposition of Re. For example, for a ratio of $\text{Ni}^{2+}/\text{ReO}_4^- = 2.7/1$ in the solution, an alloy containing ~65 atom % of Re is obtained. When the above ratio is reduced to unity, the concentration of Re in the alloy increases to 93 atom %. The FE decreases with increasing concentration of Re in the alloy because Re is a better catalyst than Ni for the hydrogen evolution reactions.

3. Except at low concentrations of the perrhenate ion, ReO_4^- , where mass-transport limitation of this ion may play a role, the composition of the alloy and the partial current densities for deposition of Re and Ni are essentially independent of the concentration of ReO_4^- , indicating that this anion does not take part in the rate-determining step for deposition of the alloy.

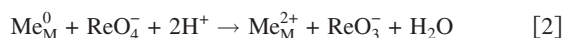
4. In contrast, the rate of Ni deposition, for example, increases sharply with increasing concentration of Ni^{2+} in the solution. This is accompanied by an increase in the FE and a decrease in the Re content of the alloy. The partial current density for deposition of Re also increases with the concentration of Ni^{2+} , indicating that nickel ions serve as catalysts in the deposition of Re.

5. The above applies also to Co^{2+} and Fe^{2+} , although to different degrees, showing that each of the above iron-group metals can act as a catalyst for the deposition of Re.

Based on the above findings, a mechanism was proposed on the basis of the idea that the iron-group metal, Me, acts as a mediator in the (partial) reduction of the ReO_4^- ion. The critical step in this mechanism is assumed to be



followed by



The purpose of the present article is to lend further support to the above mechanism by showing directly that all three iron-group metals can reduce ReO_4^- at open circuit either to a lower valence oxide or to the free metal.

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Experimental

The experiments reported here consisted of placing each of the iron-group metals in a 343 mM solution of citric acid adjusted to pH 5.0 ± 0.1 with NaOH. Metal foils or thin films plated in situ on a copper substrate were employed. The thin films were formed by electroplating at $i = 50 \text{ mA cm}^{-2}$ for $t = 10 \text{ min}$ in a solution that did not contain ReO_4^- . In the next step, NH_4ReO_4 was added in the amount needed to reach a final concentration of 34 mM of ReO_4^- and the solution was kept at $70.0 \pm 0.1^\circ\text{C}$ for an hour to allow chemical reaction between the metal and the ReO_4^- ion to take place. Subsequently, the samples were washed and the nature of the species in the deposits was analyzed using a high resolution X-ray photoelectron spectroscopy (HR-XPS). This was performed in ultrahigh vacuum (2.5×10^{-10} Torr base pressure) using a 5600 Multi-Technique System (PHI, MN). The samples were irradiated with an Al $K\alpha$ monochromated source (1486.6 eV), and the outcome electrons were analyzed by a spherical capacitor analyzer using the slit aperture of 0.8 mm. The samples were analyzed either at the surface or after sputter cleaning (sputter rate on SiO_2/Si was ~4.3 nm/min). The binding energy of adventitious carbon at 285 eV was taken as an energy reference for all measured peaks. High resolution spectra were taken at pass energy of 11.75 eV at increments of 0.05 eV/step to allow precise energy position and peak shape determination. Curve-fitting was done with Gaussian-Lorentzian function by using a 5600 Multi-Technique System software. Two fitting parameters, namely peak position and full width at half-maximum, were fixed within less than about $\pm 0.4 \text{ eV}$. Such accuracy seems to be reasonable in light of the complexity of the measured Re 4f spectral curve.⁴ The Re 4f doublet components separation was kept constant at 2.43 eV, and the component intensity ratio was kept at 3:4, as normally expected for the splitting of this level.

All other experimental details were described in our earlier articles.¹⁻³ The process investigated was the chemical interaction of the pure metals with the ReO_4^- ion at open circuit. Thus, deposition was in effect an electroless process, testing the validity of the mechanism indicated in Eq. 1 and 2 above.

Results and Discussion

The HR-XPS data for the selected samples, including the binding energies of the analyzed peaks, are summarized in Table I, and the corresponding spectra and curve-fitting are shown in Fig. 1 and 2. The different oxides were determined on the basis of the HR-XPS curve-fitting of the spectrum observed and the data from several works.⁵⁻⁷ Our XPS results agree well with those obtained by Cimino et al.,⁵ presented in Table II for comparison. Perrhenate and its corresponding oxide Re_2O_7 were also detected on the surface of several samples. After sputter cleaning, the chemical composition of the coating changed. However, this might be influenced by a preferential sputtering effect typical of heavy metal oxides that causes oxygen depletion and appearance of lower oxidation states of Re.^{4,6,8}

Table I. The content and binding energies of rhenium and its oxidation states, as determined from HR-XPS data curve-fitting before and after sputtering (Re + Me = 100 atom %, where Me = Fe, Ni, or Co).

Sample no.	Re in different oxidation states						
	Oxidation states	Before sputtering Re 4f _{7/2} (eV)	Content (atom %)	States	After sputtering Re 4f _{7/2} (eV)	Content (atom %)	
211 (substrate: Fe foil)			20.0 total	Curve is not fitted (see text)		20.0 total	
	Re	—	—				
	ReO ₂	42.6	8.9				
	Re ₂ O ₅	43.7	2.0				
	ReO ₄ ⁻	46.3	7.3				
230 (substrate: Ni foil)			—	Curve is not fitted (see text)		0.03 total	
	Re	—	—				
	ReO ₂	42.6	8.9				
	Re ₂ O ₅	43.7	2.0				
	ReO ₄ ⁻	46.3	7.3				
213 (substrate: thin film of Ni on Cu)			2.9 total	Re Re–Ni alloy		2.0 total	
	Re	40.9	1.1		Re	40.7	1.44
	ReO ₂	42.2	0.8		Re–Ni alloy	41.1	0.56
	ReO ₃	44.3	0.3				
	ReO ₄ ⁻	46.0	0.7				
234 (substrate: thin film of Co on Cu)			1.3 total	Re Re–Co alloy		1.1 total	
	Re	40.9	0.08		Re	40.7	0.8
	ReO ₂	42.2	0.40		Re–Co alloy	41.1	0.3
	Re ₂ O ₅	43.5	0.20				
	ReO ₃	44.7	0.15				
	ReO ₄ ⁻	46.4	0.42				
	Re ₂ O ₇	47.0	0.05				

Next, we list the HR-XPS results obtained for each of the three iron-group metals.

Iron.—When an iron foil was immersed in a solution of citric acid at pH 5, no reactions seemed to occur and the solution remained clear and colorless. Upon addition of ReO₄⁻, however, vigorous corrosion of iron was observed and the solution turned black due to the corrosion products in the solution. This showed, beyond any doubt, that the ReO₄⁻ ion was being reduced by metallic iron. A similar phenomenon of enhancement of the corrosion of iron in the presence of perrhenate was reported by Szabó and Bakos.⁹ The analysis of the surface by HR-XPS shown in Fig. 1a reveals Re oxides, but no metallic Re on the Fe foil substrate (sample no. 211). The main reduction product was ReO₂. A doublet with a binding energy of Re 4f_{7/2} peak at 43.7 eV was detected, for which no data have been reported so far. Its binding energy is higher than that of ReO₂ and lower than that of ReO₃, so it is concluded that this doublet corresponds to the five-valence oxide Re₂O₅, which has not been detected before by XPS, to our knowledge.

The metallic Re was detected as the predominant component in addition to Re oxides after 6 min of sputtering (not presented here). A similar experiment with a thin Fe film plated on a Cu substrate (sample no. 235) could not be analyzed by HR-XPS because the iron thin film corroded too fast.

Nickel.—Electroless deposition on Ni foil (sample no. 230) did not reveal Re signal on the surface, probably because the native oxide of Ni was either not removed completely or it was regenerated in the solution upon immersion. 0.03 atom % of Re appeared after 2 min of sputtering only. No HR-XPS measurements were done on this sample because of the small quantity of Re. However, when a thin film of Ni electrodeposited in situ on a copper substrate was used (sample no. 213), chemical reaction occurs and analysis by HR-XPS yields 1.05 atom % metallic Re in addition to several Re oxides, as shown in Fig. 1b and Table I. A new doublet appears in addition to metallic Re after sputtering. It cannot be identified as a Re oxide because its binding energy is too close to that of metallic Re. This doublet may represent a Re–Ni alloy. The spectrum of

sample no. 213 after 4 min of sputtering is presented in Fig. 2a. Possibly, some quantity of Re–Ni alloy was present on the surface of this sample before sputtering as well. However, the alloy component was not taken into consideration in curve-fitting before sputtering due to the complexity of the measured curve.

Cobalt.—A thin film of Co deposited on a Cu substrate (sample no. 234) gave rise to results similar to those obtained for the Ni film. Although the total amount of Re found was lower, the analysis by HR-XPS yields metallic Re in addition to a large variety of Re oxides, as shown in Fig. 1c and Table I. A doublet with the same binding energy as that of Re–Ni alloy of sample no. 213 was detected in addition to metallic Re after sputtering. This doublet may represent a Re–Co alloy. The spectrum of sample no. 234 after 10 min of sputtering is presented in Fig. 2b. Possibly, some quantity of Re–Co alloy was present on the surface of this sample before sputtering as well, similar to sample no. 213. The ratio between metallic Re and Re alloy after sputtering was about 2.6–2.7 for both Re–Ni and Re–Co alloys (samples no. 213 and no. 234, respectively).

The above results present clear evidence that the iron-group metals, Ni, Fe and Co, can reduce ReO₄⁻ chemically to a less stable ion or a lower valence oxide adsorbed on the surface. This supports our proposed mechanism presented in Eq. 1 and 2 above and in our previous articles.^{1–3} This mechanism stipulates that the addition of Me²⁺ to the plating bath increases the rate of Re deposition through a unique mechanism involving Me⁰ atoms formed by electroplating, followed by the chemical reduction of ReO₄⁻ to a less stable ion or possibly to metallic Re. Comparing the three different iron-group metals, Ni produced more metallic Re than Co, whereas Fe reduced the perrhenate only to lower valence oxides but not to metallic Re.

The fast rate of corrosion of iron at open circuit in the presence of the ReO₄⁻ anion poses no problem in the electroplating of Re–Fe alloys because during plating, the potential is held at a highly negative value that apparently reduces the rate of corrosion of Fe.

Despite the results reported herein, two questions remain unanswered:

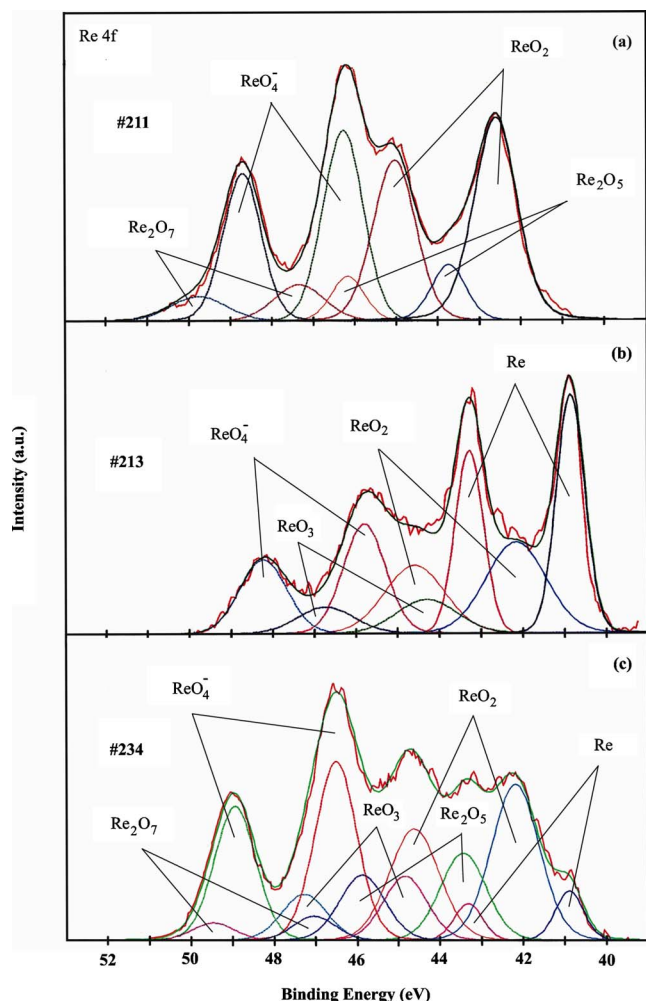


Figure 1. (Color online) Normalized high resolution Re 4f XPS spectra of different samples before sputtering: (a) Fe foil substrate (sample no. 211), (b) thin film of Ni on Cu substrate (sample no. 213), and (c) thin film of Co on Cu substrate (sample no. 234).

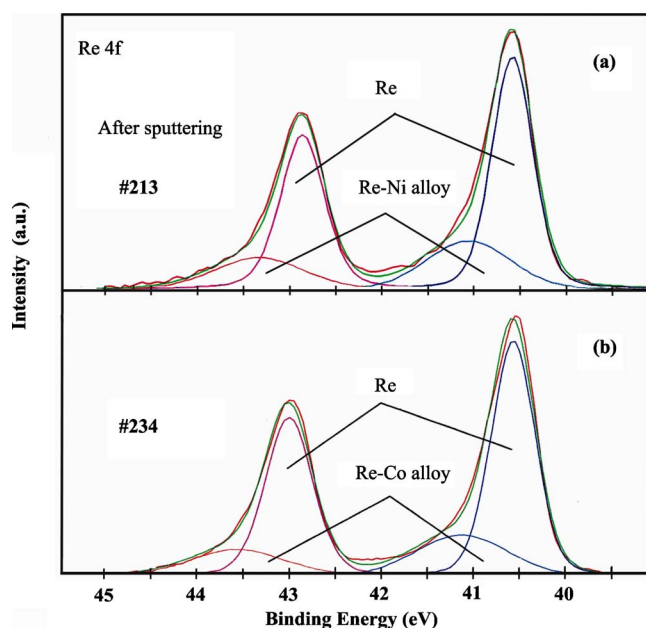


Figure 2. (Color online) Normalized high resolution Re 4f XPS spectra of different samples after sputtering: (a) Thin film of Ni on Cu substrate (sample no. 213) and (b) thin film of Co on Cu substrate (sample no. 234).

Table II. The binding energies of rhenium and its oxidation states given in Ref. 5 (as measured with two different spectrometers: first column corresponds to AEI ES 100, whereas the second column is measured by VG 3).

Re	40.7	40.9
ReO ₂	42.5	42.5
Re ₂ O ₅	—	—
ReO ₃	44.5	44.5
ReO ₄ ⁻	46.3	46.5
Re ₂ O ₇	46.9	47.1

1. Is the ReO₄⁻ ion reduced chemically during electroplating of Re–Me alloys only to the ReO₃⁻ ion, which is then reduced further electrochemically to metallic Re, or is it reduced chemically directly to a lower valence oxide (for example, to ReO₂, which was detected by our HR-XPS measurements) or even to metallic Re? In the latter case, this could be considered to be a unique type of electroless deposition in which the reducing agent is continuously regenerated in situ.

2. Is nickel deposited in parallel to deposition of Re–Me alloy during electroplating or does it act only as a catalyst? The observation that the ratio of Re/Ni in the alloy is 2/1 when the ratio of the corresponding elements in the plating bath is 1/3 indicates that the Me²⁺ ion acts as a catalyst with several turnovers in which Me²⁺ is reduced electrochemically to Me⁰ and then reoxidized chemically to Me²⁺ during electroplating. Thus, although elemental analysis determined by energy-dispersive X-ray spectroscopy shows that both Ni and Re exist in the electroplated film, this may not be a real alloy deposition process. Instead, Re could be the metal being electroplated and Me is only occluded in the deposit because the rate of its reoxidation according to Eq. 2 is too slow compared to the rate of deposition of Re. Would this be the case, there should be a way to catalyze the rate of deposition of Re with little or no inclusion of Me in the deposit by fine tuning the solution chemistry.

Conclusions

In this article, supporting evidence to our suggested mechanism for deposition of Me–Re alloys is presented. ReO₄⁻ can be reduced chemically at open circuit to lower valence oxides and to metallic Re by each of the iron-group metals. This can explain the catalytic effect that the iron-group metals have on the electrodeposition of Re. In these open-circuit measurements, nickel was a better reducing agent than cobalt and iron was the worst reducing agent among the three.

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