

## CHAPTER 6

### ANODIC STRIPPING ANALYSIS OF TITANIUM

Solutions containing Ti (IV) and Ti (III) in various concentrations of HBr and KBr (80) and in 7 - 10 M  $H_2SO_4$  (81) were polarographically studied. The reduction of titanium in  $H_3PO_2$  (82), in diethanolaminophosphonic acid (83), and in  $1 \times 10^{-3}M$  thiocyanate solution (84) at a dropping mercury electrode were described. Polarographic determination of titanium was reported in the mixture of titanium and tungsten using 10 N  $H_4P_2O_7$  as the supporting electrolyte (85); in tantalum and niobium ores using the electrolyte containing 5.4 M  $H_2SO_4$  and 0.2 M  $K_2S_2O_7$  (86); in niobium metal and oxide using 13 - 14 N  $H_4P_2O_7$  as the supporting electrolyte (87); in lead zirconate-lead titanate ceramic powders using the electrolyte containing 0.5 M ammonium acetate - 0.1 M acetic acid - 0.1 M EDTA (88); and in  $H_2SO_4$  using  $KClO_3$  or  $KBrO_3$ -EDTA solution as the supporting electrolyte (89). The effect of various polyols (90) and vanillin (91) on the polarographic reduction of Ti (IV) in HCl was examined. In addition, Ti (III) was polarographically oxidized in 1 N  $H_2SO_4$  (92), and in malonic acid, glycolic acid, succinic acid, ethylenediamine hydrochloride - hydrazine monohydrochloride (93).

The determination of Ti (IV) by ac polarography was possible in citrate buffer of pH 1.6 containing 0.01% dodecylamine (94) and in  $H_3PO_4$  (95). The oxidation of titanium in aqueous sodium nitrite solution by ac polarography was reported (96). Moreover, amperometric titration of Ti (IV) with EDTA was performed by dc and ac

polarography (97).

## 6.1 Evaluation of Electrolyte

### 6.1.1 Sulfuric acid

Since the stock solution of Ti (IV) was prepared in 0.5 M and 1.0 M  $\text{H}_2\text{SO}_4$ , the use of  $\text{H}_2\text{SO}_4$  as a supporting electrolyte is examined. No cathodic peak is shown in the cathodic voltammogram of  $1.00 \times 10^{-4}$  M Ti (IV) in 0.5 M, 1.0 M, and 6.0 M  $\text{H}_2\text{SO}_4$ , however, a cathodic peak of the system in 8 M  $\text{H}_2\text{SO}_4$  occurs at ca. +0.03 V and in 10 M  $\text{H}_2\text{SO}_4$  occurs at ca. -0.07 V, respectively. After 10-minute-electrodeposition of  $1.00 \times 10^{-4}$  M Ti (IV) in 8 M or 10 M  $\text{H}_2\text{SO}_4$  at -0.10 V, no anodic peak is obtained in the stripping voltammogram.

### 6.1.2 0.2 M citric acid and citrate buffer

The cathodic voltammogram of  $1.00 \times 10^{-4}$  M Ti (IV) in 0.5 M  $\text{H}_2\text{SO}_4$  and 0.2 M in citric acid gives no cathodic peak. Thus, the reductions of Ti (IV) both in 0.5 M  $\text{H}_2\text{SO}_4$  and 1.0 M  $\text{H}_2\text{SO}_4$  are studied in the citrate buffer (0.2 M citric acid -0.2 M ammonium citrate system) at pH 1.2 and 5.9. Neither system gives a cathodic peak.

### 6.1.3 McIlvaine buffer (0.1 M citric acid -0.2 M $\text{Na}_2\text{HPO}_4$ system)

The solution of  $1.00 \times 10^{-4}$  M Ti (IV) in 0.5 M  $\text{H}_2\text{SO}_4$  and in McIlvaine buffer of pH 2.4 or 3.0 give no cathodic peak. In

the pH higher than 3.0 of McIlvaine buffer, Ti (IV) is precipitated and no cathodic voltammogram is performed.

#### 6.1.4 $\text{Na}_2\text{HPO}_4$ and 0.1 M $\text{Na}_2\text{HPO}_4$ -0.1 M ammonium citrate system

Ti (IV) in 0.5 M  $\text{H}_2\text{SO}_4$  is precipitated in 0.1, 0.5, and 1.0 M  $\text{Na}_2\text{HPO}_4$  and in 0.1 M  $\text{Na}_2\text{HPO}_4$  -0.1 M ammonium citrate. Therefore, no cathodic voltammetry of Ti (IV) in these systems is attempted.

#### 6.1.5 KCl-HCl system

The composition of KCl and HCl in the system is varied as shown in Table 10. A small cathodic peak of  $1.00 \times 10^{-4}$  M Ti (IV) in either the 0.1 M KCl -0.1 M HCl system or the 0.2 M HCl-0.1 M KCl system is shown at -0.50 V. The electrodeposition of Ti (IV) in both systems is performed at -0.60 V for 20 minutes. No anodic peak is observed in the anodic stripping voltammogram of both systems.

#### 6.1.6 Other electrolytes

Cathodic voltammetry of Ti (IV) in 0.5 M  $\text{H}_2\text{SO}_4$  or 1.0 M  $\text{H}_2\text{SO}_4$  is investigated in the following electrolytes: 1, 3, and 6 M  $\text{H}_3\text{PO}_4$ , 0.2 M acetic acid-0.2 M sodium acetate, 0.2 M acetic acid-0.2 M sodium acetate -0.07 M EDTA, and acetate buffer at pH 1.4. No cathodic peak is shown. In addition, cathodic voltammograms of Ti (IV) in 1.0 M  $\text{H}_2\text{SO}_4$  and 6.0 M  $\text{H}_2\text{SO}_4$  are performed in 0.1 M  $\text{KHSO}_4$ , in 1 M  $(\text{NH}_4)_2\text{SO}_4$ , and in 2 M  $\text{NH}_4\text{Cl}$ . No cathodic peak is observed.

Table 10 The cathodic behavior of  $1.00 \times 10^{-4}$  M Ti (IV)  
in 0.5 M  $H_2SO_4$  and the KCl-HCl system.

Conc (M)		$E_{p,c}$ (V)	Remark
HCl	KCl		
0.05	0.1	none	{ very small peak, $i_c$ cannot be measured
0.1	0.1	-0.50	
0.2	0.1	-0.50	
0.5	0.1	none	
2.0	0.1	none	
2.0	0.1	none	
4.0	0.1	none	
6.0	0.1	none	
0.1	0.2	none	
0.1	0.5	none	
0.1	2.0	none	
0.1	4.0	none	

## 6.2 Stripping analysis

Since no anodic peak of Ti (IV) in the electrolytes investigated illustrates in the anodic stripping voltammogram, the anodic stripping analysis of Ti (IV) in these electrolytes is not performed.

## CHAPTER 7

### CONCLUSION AND RECOMMENDATION

Anodic stripping analysis of Mo (VI), W (VI), V (V), and Ti (IV) are investigated at a glassy carbon electrode in the present study. Since the metal ions interested are multivalent ions, the cathodic reaction of these ions could yield a single or many reducing products at the electrode surface. Thus, many supporting electrolytes and the electrodeposition potential for each ion are studied in order to obtain a single cathodic species. Even a single reducing product is obtained in the electrodeposition step, a single or many oxidizing species could be yielded in the stripping step. To avoid many anodic species resulted, the electrodeposition time is changed. Not only the different supporting electrolytes are used but also the concentration of the supporting electrolyte and the pH of test solution are varied in order to produce the highest sensitivity for the analysis of each ion. The optimum conditions for anodic stripping analyses of Mo (VI), W (VI), and V (V) are concluded in Table 11. Owing to the technique used is for trace analysis, the concentration range of  $10^{-4}$  M and below are of interest.

By this study, Mo (VI) in 0.02 M acetic acid -0.02 M sodium acetate -0.10 M NaCl results a cathodic peak at -0.68 V, after electrodeposition at -0.80 V an anodic peak is obtained at -0.25 V, and the anodic peak current is dependent on the Mo (VI) concentration. However, W (VI) in this supporting electrolyte gives a cathodic peak at -1.37 V, after electrodeposition at -1.40 V no anodic peak

Table 11 Conditions for anodic stripping analysis of some nonferrous metals.

Analyte	Supporting electrolyte	$E_{p,c}$ (V)	Deposition		Conc range (M)	$E_{p,a}$ (V)	Comments
			Potential (V)	Time (min)			
Mo (VI)	0.02 M acetic acid -0.02 M sodium acetate -0.10 M NaCl	-0.68	-0.80	5	$1.00 \times 10^{-4}$ - $1.00 \times 10^{-5}$	-0.25	linear dependence of concentrations on peak currents
				10	$1.00 \times 10^{-5}$ - $2.00 \times 10^{-6}$		
W (VI)	0.02 M acetic acid -0.004 M sodium acetate at pH 3.0	-1.90	-2.00	5	$1.00 \times 10^{-4}$ - $2.00 \times 10^{-5}$	-0.20	nonlinear propor- tionality of peak currents to concentra- tions
				10	$1.00 \times 10^{-4}$ - $5.00 \times 10^{-5}$	-0.16	linear dependence of concentrations on peak currents
				20	$1.25 \times 10^{-5}$ - $2.50 \times 10^{-6}$	+0.04	
V (V)	0.2 M HCl -0.2 M $NH_4OH$ at pH 4	-0.38	-0.50	5	$4.00 \times 10^{-4}$ - $8.00 \times 10^{-5}$	+0.16	linear dependence of concentrations on peak currents
				10	$4.00 \times 10^{-5}$ - $6.00 \times 10^{-6}$	-0.14	
				20	$6.00 \times 10^{-6}$ - $1.00 \times 10^{-6}$	-0.18	

is shown in the first anodic voltammogram but an anodic peak at  $-0.84$  V is observed in the second and third anodic voltammogram and the peak current cannot be measured due to the high charging current in the anodic voltammetry. As well as V (V) and Ti (IV) give no cathodic peak in the above supporting electrolyte. Thus, it seems that Mo (VI) could be determined quantitatively in the presence of W (VI), V (V), and Ti (IV) by using  $0.02$  M acetic acid  $-0.02$  M sodium acetate  $-0.10$  M NaCl as supporting electrolyte. An advanced project for anodic stripping analysis of Mo (VI) in the mixture of Mo (VI), W (VI), V (V), and Ti (IV) in this electrolyte is suggested for further study.

As Ti (IV) is hardly reduced in many electrolytes examined (see pp. 43 - 4) the anodic stripping analysis of Ti (IV) is impossible in the present study. Since the dc and ac polarographic oxidation of Ti (III) are possible (92, 93, 96), the cathodic stripping analysis of titanium would be another interesting project.

Finally, further study of the reduction product of W (VI) after 5-minute-electrodeposition would clarify the mechanism of the electrode process in resulting nonlinear dependence of anodic peak currents on concentrations ( see Table 7 and Figure 5A ).