

## REDUCTION OF VANADATE IN H<sub>2</sub>SO<sub>4</sub> AT COPPER CATHODE

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### ABSTRACT

The electrochemical reduction of vanadate at copper cathode has been studied and it has been found that a current efficiency of 35-39% only could be achieved for the V (IV) stage. The galvanostatic experiments show three stages before hydrogen evolution. Cyclic voltammograms gave two peaks at different sweep rates; the first peak occurring between 400 and 300 mv and the second peak between 775 and 750 mv or 675 and 650 mv with sweep rates ranging from 500 mv. sec<sup>-1</sup> to 20 mv. sec<sup>-1</sup> respectively.

Key words: Vanadate, electroreduction, cyclic voltammograms.

### INTRODUCTION

The compounds of vanadium offer an interesting study because of the existence of its derivatives in four valency states as well as their use both in preparative and analytical applications. Though the pentavalent vanadium compounds can be reduced to lower valency states by chemical methods, electrolytic method offers certain advantages for the same. Literature survey shows that pentavalent vanadium compounds could be reduced with a number of metals like mercury, platinum, gold or pyrolytic graphite, either at controlled potentials or by polarographic techniques in acid, alkaline or neutral medium [1-15]. Depending on the metal used for the cathodic reduction of V (V), different valency states of vanadium compounds could be obtained.

The present paper deals on the electroreduction of ammonium meta-vanadate in sulphuric acid solution at copper cathode in a diaphragm cell to obtain vanadium compound in 4-valency state. In addition, preliminary studies on steady state galvanostatic polarization measurements and cyclic voltammetric measurements are also included.

### EXPERIMENTAL

#### Cell assembly

A cylindrical vessel (500 ml capacity) made of glass, in which porous pot (3 cm dia x 11 cm ht) was kept, acted as the electrolytic cell. While polished copper rod (1 cm dia x 15 cm ht) was used as cathode, perforated lead sheet (2 cm x 11 cm) made into a cylindrical form and kept in porous pot, acted as anode. The cell assembly was kept in an outer vessel filled with water and the same was heated or cooled for controlling the temperature ( $\pm 1^\circ\text{C}$ ) of the electrolytic cell. Ammonium meta-vanadate solution (0.1 M) along with different concentrations of sulphuric acid was taken as catholyte and 5 N sulphuric acid was employed as anolyte.

#### Electrolysis

By employing a constant current source (max. 1 A) the electrolysis was carried out by passing theoretical quantity of electricity for the reduction of V (V) (IV). After the electrolysis, the catholyte was estimated for V (V) and V (IV) and anolyte for diffused catholyte available in the form of V (V).

#### Cell assembly for galvanostatic and cyclic voltammetry experiments

An all-glass H-shaped cell assembly with porous sintered disc to separate the

anode and cathode compartments was used for both galvanostatic and cyclic voltammetric measurements. Copper planar electrode (1 cm<sup>2</sup> area) was employed as anode. Deaeration was done by bubbling purified nitrogen gas through the solution. All the measurements were done against saturated calomel electrode (SCE) using a bridge filled with ammonium meta-vanadate saturated potassium chloride solution. For galvanostatic steady state measurements, a constant current source was employed. A potentiostat coupled with a scan generator and x-y/t recorder were used for the measurement of cyclic voltammograms.

#### Analysis

Ammonium meta-vanadate in sulphuric acid was estimated by titrating against a standard ferrous ammonium sulphate solution employing potentiometric technique. The reduced vanadium (IV) was estimated by potentiometric titration with a standard solution of ceric sulphate [16,17].

### RESULTS AND DISCUSSION

The variation of current efficiency with cathode current density (varying from 0.1 to 4 A.dm<sup>-2</sup>) for copper cathode under different sulphuric acid concentrations (1 N to 10 N) is shown in Table I. It is seen from the results that the current efficiency decreases with current density under all acid concentrations. The current efficiency, though low (i.e. 35-39% for most of the conditions), is almost constant between 0.25 and 1 A.dm<sup>-2</sup> for all acid concentrations studied. It is also observed that the variation of acid concentration has no significant influence on current efficiency for any given current density except with 10 N-acid where there is a pronounced decrease in efficiency. There appears to be a marked decrease in current efficiency at 4 A.dm<sup>-2</sup> for the change in acid concentration from 2N to 10 N.

The effect of temperature on current efficiency during the reduction of vanadate solution at copper cathode is given in Table II. The results indicate that the current efficiency increases from 37% to 42% with the increase of temperature from 30°C to 60°C, thereby indicating the employment of higher temperature to be favourable for the reaction.

Employing the favourable conditions arrived at with copper cathode for the electrolytic reduction of vanadate, the reduction has been carried out with different cathode materials having varied values of hydrogen overvoltage and the results are presented in Table III, which indicate that the maximum current efficiency is given by copper or amalgamated copper cathode. Though one can expect the reduction of vanadate not only to 4-valency state but also still lower valency states with the electrodes like lead, mercury etc., having high hydrogen overvoltage, the analytical results confirmed the absence of V (III) and V (II) compounds under the conditions employed.

**Table I: Effect of current density on current efficiency at different acid concentrations**Temp: 29 ± 1 °C; Cu Cathode, 0.15 dm<sup>2</sup> exposed area; 0.10 M NH<sub>4</sub> VO<sub>3</sub>; 150 ml solution

H <sub>2</sub> SO <sub>4</sub> (N)	Current density (A.dm <sup>-2</sup> )	Current efficiency (%)	Average voltage (V)	Energy efficiency Watt-hr
1 N	0.1	39.0	1.76	0.37
	0.25	35.5	2.18	0.45
	0.5	35.4	2.31	0.48
	1	35.1	2.42	0.51
	2	34.6	2.80	0.54
2 N	0.1	37.8	2.07	0.43
	0.25	35.7	2.27	0.47
	0.5	35.7	2.33	0.49
	1	34.2	2.47	0.52
	2	34.0	2.56	0.54
4 N	0.1	38.5	2.05	0.43
	0.25	36.7	2.24	0.46
	0.5	35.2	2.25	0.47
	1	35.2	2.36	0.49
	2	32.1	2.47	0.52
5 N	0.1	38.7	2.02	0.43
	0.25	35.5	2.28	0.48
	0.5	35.1	2.32	0.49
	1	35.1	2.40	0.51
	2	34.0	2.51	0.52
10 N	0.1	34.8	2.01	0.42
	0.25	39.2	2.20	0.47
	0.5	33.4	2.24	0.48
	1	33.1	2.40	0.53
	2	32.0	2.51	0.54
10 N	4	23.7	2.68	0.55

**Table II: Effect of temperature on current efficiency**(Other conditions same as in Table I); 0.12 M NH<sub>4</sub> VO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub>; 1 A.dm<sup>-2</sup>

Temperature (°C)	Current efficiency (%)	Average voltage (V)	Energy efficiency Watt-hr
30°	37.0	2.55	0.62
40°	38.5	2.38	0.58
50°	39.5	2.36	0.57
55°	40.5	2.35	0.57
60°	42	2.33	0.57

**Galvanostatic polarisation measurement**

The electrolytic reduction of vanadate solution was carried out using a copper cathode under steady state conditions and the results are shown in figure 1. It is observed from the figure that the range of current density increases with vanadate concentration. At 0.05 and 0.1 M vanadate

concentration, there appears to be three distinct stages before hydrogen evolution takes place at about -750 and -800 mV vs SCE. These may be attributed to the reduction of V(V) to different lower valency states upto V(II). However in dilute solutions, the reduction of V(V) may be taking place with the intermediate steps being not so well pronounced.

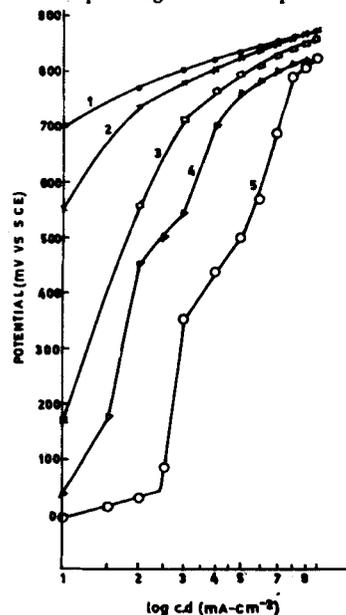
**Figure 1: Galvanostatic polarisation curves during the reduction of different concentrations of metavanadate in 1 N H<sub>2</sub>SO<sub>4</sub> at cu cathode.**1) 1 NH<sub>2</sub>SO<sub>4</sub> (Pure) 2) 0.01 M 3) 0.025 M 4) 0.05 M 5) 0.10 M  
**Cyclic voltammetry**

Figure 2 (a) and (b) show the results of cyclic voltammetry under different scan rates (20 to 500 mV sec<sup>-1</sup>) employing 0.1 M ammonium meta vanadate and 1 N H<sub>2</sub>SO<sub>4</sub> as electrolyte at copper electrode and room temperature. The voltammograms indicate two well pronounced peaks for cathodic reactions for all sweep rates. The potentials at which the two peaks are observed for different scan rates (i.e. Ep<sub>1</sub> and Ep<sub>2</sub>) are shown in Table IV. It is seen that there is a shift in peak potential for the first peak from 400 to 300 mV (vs SCE) for scan rates from 500 to 20 mV sec<sup>-1</sup>. The shift of peak potential to more negative values with increase of sweep rate indicates that the reaction occurring is significantly irreversible. For the second peak, the shift is not appreciable. In the reverse cycle the anodic peak is obtained at 475–480 mV at all sweep rates. The first peak may be attributed to the reduction of V(V) to V(IV) and the second peak for the reduction of V(IV) to V(II) since similar observations have also been made in polarography [2,4]. This is

**Table III: Effect of cathode materials on current efficiency (conditions same as in Table I)**

Temp: 29 ± 1 °C

Cathode employed	Current efficiency (%)	Average voltage (V)	Energy efficiency Watt-hr
Platinum	22.0	2.45	0.60
Copper	37.0	2.55	0.62
Lead	29.5	3.02	0.73
Cadmium	29.0	3.18	0.77
Cu amalgamated	36.4	3.14	0.76
Pb amalgamated	29.3	3.00	0.73
Cd amalgamated	26.5	2.94	0.71

further supported by conducting a cyclic voltammetry experiment with V (IV) and figure 3 shows the voltammogram for the same at copper cathode under a sweep rate of 100 mV.sec<sup>-1</sup>. The absence of first peak clearly indicates that the first peak obtained with V (V) is due to the reduction of V (V) to V (IV). The peak potential of figure 3 corresponds to the second peak potential of figure 2 (a) and (b). As the theoretical potential of V (II) formation is nearer to the second peak potential of figure 2 (a) and (b) or the peak potential of figure 3, it may be assumed that the second peak is due to the formation of V (II). The anodic peak of figure 3 also corresponds to the anodic peaks of figure 2 (a) and (b) showing the oxidation of V (II) to higher oxidation state.

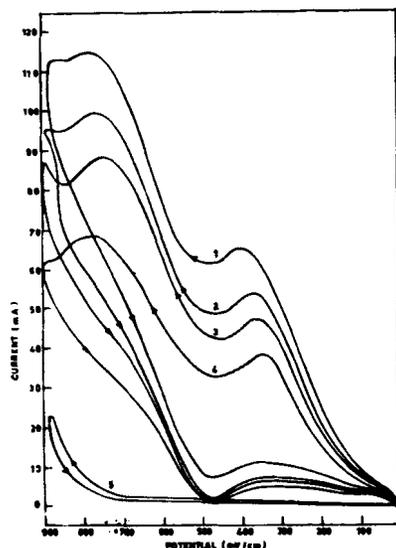


Fig. 2 (a) Cyclic voltammograms using V(V) in 1 NH<sub>2</sub>SO<sub>4</sub>: 1) 500 2) 400 3) 300 4) 200 5) 500 for pure H<sub>2</sub>SO<sub>4</sub>

#### Cyclic voltammetry

Figure 2 (a) and (b) show the results of cyclic voltammetry under different scan rates (20 to 500 mV sec<sup>-1</sup>) employing 0.1 M ammonium meta vanadate.

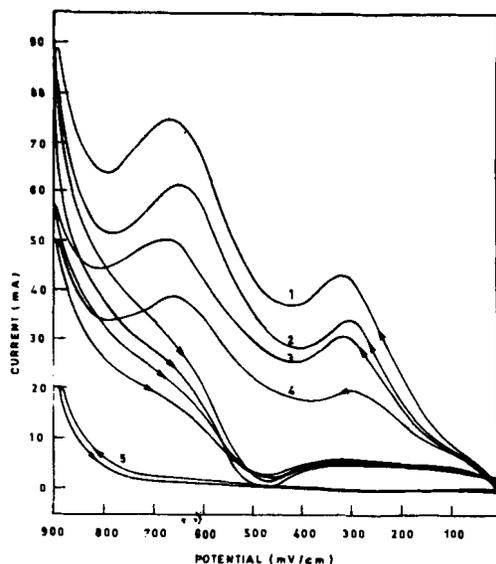


Fig. 2 (b) Cyclic voltammograms using V(V) in 1 NH<sub>2</sub>SO<sub>4</sub> under different sweep rates. (mv sec<sup>-1</sup>): 1) 150 2) 100 3) 50 4) 20 5) 150 for pure H<sub>2</sub>SO<sub>4</sub>

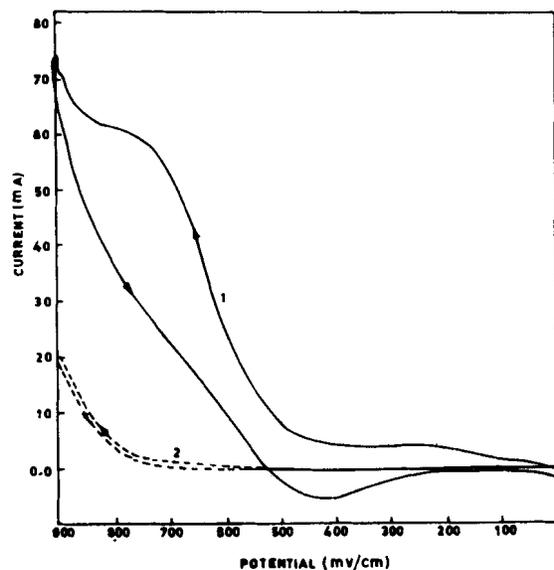


Figure 3: 1) Cyclic voltammograms using V(IV) in 1 NH<sub>2</sub>SO<sub>4</sub> at 100 mV. sec<sup>-1</sup> 2) with 1 NH<sub>2</sub>SO<sub>4</sub> at the same sweep rate.

Table IV: Ep<sub>1</sub> and Ep<sub>2</sub> for different scan rates

Scan rate (mV. sec <sup>-1</sup> )	Ep <sub>1</sub> (mV)	Ep <sub>2</sub> (mV)	Anodic peak (mV)
500	400	775	475
400	370	770	475
300	360	750	475
200	350	750	480
150	325	675	480
100	320	650	480
50	320	650	475
20	300	650	475

#### CONCLUSIONS

The reduction of vanadate to V (IV) stage at copper cathode gives about 35-39% current efficiency. The galvanostatic experiments show that there are three distinct stages before hydrogen evolution of higher concentrations viz. 0.05 and 0.1 M ammonium meta-vanadate in 1 N H<sub>2</sub>SO<sub>4</sub>. The preliminary experiments with cyclic voltammetry show two peaks with different scan rates from 20 mV. sec<sup>-1</sup> to 500 mV. sec<sup>-1</sup>

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