ELECTRODICS AND ELECTROBIOLOGY

VOLTAMMETRIC BEHAVIOUR OF SULPHATE AND OXALATE COMPLEXES OF Ti⁴⁺/Ti³⁺ REDOX SYSTEM ON COPPER ELECTRODE

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ABSTRACT

The cyclic voltammetric studies of the sulphate and oxalate complexes of Ti^{4+}/Ti^{3+} redox systems on Cu electrodes are reported and the results are compared with the behaviour on Hg and GC electrodes reported earlier. The easily reducible sulphate complexes are formed only on high Ti^{4+} and H_2SO_4 concentrations as noticed in the earlier studies. The apparent heterogeneous charge transfer rate constant $(k_h{}^o)$ decreases by 40 times on Cu when compared to Hg. This rather unusual observation is probably associated with the greater blocking effect of the supporting electrolyte anions on Cu when compared to Hg. Added Cl^- as well as SO_4^{2-} exert even stronger blocking effect. The possible implication of the present study on the indirect electro-reduction technique used for the nitro compound reduction using Ti^{4+}/Ti^{3+} redox system is also discussed in some detail.

Key Words: Voltammetry, titanic oxalate, titanic sulphate, copper electrode, electron transfer kinetics

INTRODUCTION

In recent times the important role of electrode material in the electrode processes has been realised to a very great extent. A new area of 'electrocatalysis' has been developed primarily from fuel cell research [1-4]. Tailormade electrodes such as chemically modified catalytic electrodes [5-6] and conducting polymer electrodes [7-8] are being developed for catalytic purposes. Electrocatalytic effects of metal adatom monolayers on noble metal substrates [9] are also being investigated carefully. Unfortunately however all these efforts seem to focus attention on the battery and fuel-cell angle. Such search from the fundamental angle is lagging far behind in electro-synthetic work. Apart from titanium-based oxide anodes of chlor-alkali cell, [10] very little seems to have been done on the effect of electrodes in electro-organic as well as electro-inorganic synthesis.

One case in point is the technique for electroreduction of aromatic nitro compound using Ti^{4+}/Ti^{3+} redox system. Although about 20 aromatic mono an dinitro compounds [11] and even nitroso-compounds [12] have been successfully reduced to their corresponding amines on copper cathodes, using a general technique with slight modifications, the exact mechanism of this process is not known. It was thus felt desirable to investigate this reaction kinetics on copper electrode in some detail. In the present work we report the redox behaviour of Ti^{4+}/Ti^{3+} complexes alone on copper electrode in sulphuric as well as oxalic acid media. Since the voltammetric behaviour of these complexes on Hg have already been reported [13-17] and we have also discussed the voltammetric behaviour on Glassy Carbon (GC) electrodes [18,19] a comparative discussion of the interesting electrode effects on these redox processes is presented.

EXPERIMENTAL

6 mm dia electrical grade copper rod, tight-fitted into a teflon holder (99.999%), mechanically polished to mirror finish, thoroughly washed with triple distilled water and finally rinsed with tri-chloroethylene, was inserted into the H-type electrochemical cell. The electrode was then activated by cycling it up to H_2 evolution potential for at least 15 minutes in the background electrolyte (H_2SO_4 or oxalic acid). Voltammetric meaurements were then made without allowing the electrode at open-circuit conditions for longer intervals to ensure reproducibility.

Ti^{4+} solutions were prepared by dissolving titanyl sulphate salts in required amounts of H_2SO_4 or oxalic acid medium. The titanyl sulphate salt itself was prepared by heating equimolar quantities of A.R. grade TiO_2 powder and H_2SO_4 at 325-350°C for 15 minutes. More details on this procedure may be found elswhere [20].
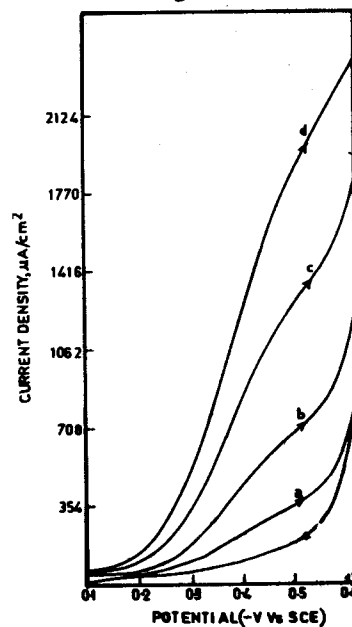

Fig. 1. Cyclic Voltammograms of Ti^{+4} - Sulphate in 2.4M H_2SO_4 At the Sweep Rate of 5 mV/sec at concentration of Ti^{+4} (a) 10 mM (b) 20 mM (c) 40 mM and (d) 60 mM

All the other details regarding the cell, and other instrumentation used are the same as described earlier [18-22]. The experiments were carried out at $25° \pm 0.5°C$ and the potentials are measured and reported vs SCE.

RESULTS

When the voltammetric experiments were carried out using low levels of Ti^{4+} concentrations (<80 mM) usually employed in cyclic voltammetric work (Fig.1) the voltammograms were not very distinct in appearance and the usual identification of peak current i_p, peak potential E_p or similar voltammetric characteristics were not possible.

However, when higher concentration of both H_2SO_4 (> 4N) and Ti^{4+} (>80mM) concentration was employed, well-defined voltammograms were obtained (Fig.2)
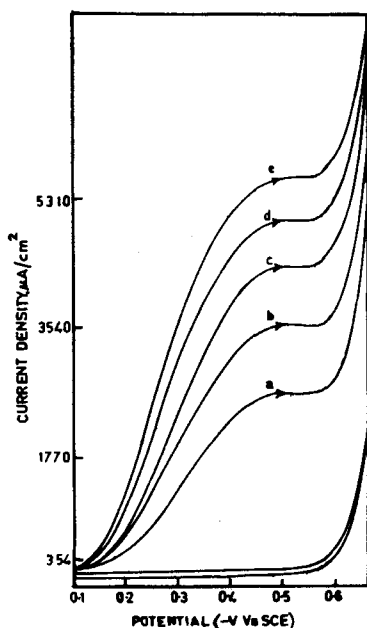

Fig. 2. Cyclic Voltammograms of Ti^{+4} - Sulphate in 2.4M H_2SO_4 at the Sweep Rate of 5 mV/sec at concentration of Ti^{+4} (a) 80 mM (b) 120 mM (c) 160 mM and (d) 200 mM (e) 240 mM

However, the peak shapes noticed usually at lower concentrations are not noticed. The voltammograms showed a limiting polarographic type of wave. The limiting current, however, increased with concentration of Ti^{4+} and square root of sweep rate, at lower sweep rates (< 40 mV/sec). At higher sweep rates, $i_p/V^{1/2}$ was found to decrease again. Within the available potential region on copper, no anodic current due to oxidation of Ti^{3+} could be noticed.

When Ti^{4+}, dissolved in oxalic acid, was considered for cyclic voltammetric experiments, well-defined CV curves with very good reproducibility were noticed (Fig.3).

The cathodic and anodic peaks were of identical height. The cathodic peak current was found to increase linearly with C_{Ti}^{4+} in the mM concentration range and with $V^{1/2}$ in a wider sweep rate range. The peak separation $(E = E_{p,a}-E_{p,c})$, however, was found to be greater than 60 mV even at low sweep rates (Table I), suggesting that the charge transfer kinetics is in the quasi-reversible region.
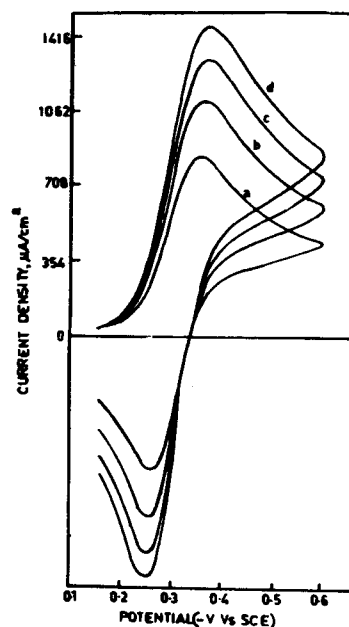

Fig.3 Cyclic voltammogram of Ti^{+4} - oxalate in 0.2M oxalic acid concentration of Ti^{+4} - 13.4 mM at sweep rates (a) 20 mV/sec (b) 40 mV/sec (c) 60 mV/sec (d) 80 mV/sec.

Table 1: Typical calculations of apparent heterogeneous charge transfer rate constants $(k_h°, _{app})$ for the oxalate complexes of Ti^{4+}/Ti^{3+} in different media on Cu cathode

System	Sweep rate $V^{1/2}sec^{-1/2}$	E_p (mv)	Ψ	$K_h° \times 10^3$ cm sec^{-1}
Ti^{4+} - oxalate	0.1414	95	0.645	2.91
(13.4 mM) in	0.2000	110	0.450	2.87
oxalic acid	0.2450	117	0.380	2.97
(0.2M)	0.2828	125	0.33	2.97
			Average	2.91
Ti^{4+} - oxalate	0.1414	180	0.153	0.689
(10.0 mM)	0.2000	215	0.096	0.612
in oxalic acid	0.2450	245	0.073	0.570
(0.2 M) and	0.2828	260	0.0656	0.591
35 mM H_2SO_4	0.3162	285	0.0508	0.612
			Average	0.615
Ti^{4+} - oxalate	0.1414	135	0.284	1.279
(13.4 mM)	0.2000	160	0.200	1.274
in oxalic acid	0.2450	180	0.153	1.194
(0.2M) with	0.2828	195	0.128	1.153
KCl (25.0 mM)			Average	1.225

To evaluate the quasi-reversible oxalate complexes in media containing H_2SO_4, the influence of smaller amounts of added H_2SO_4 on the CV behaviour of Ti^{4+}/Ti^{3+} oxalate redox system was also investigated. The CV curves still exhibit the same quasi-reversible behaviour (Fig.4). However, the peak separation now increases further (Table I). Similar effect was also noticed when KCl was added to a solution containing oxalic acid and Ti^{4+} - oxalate.
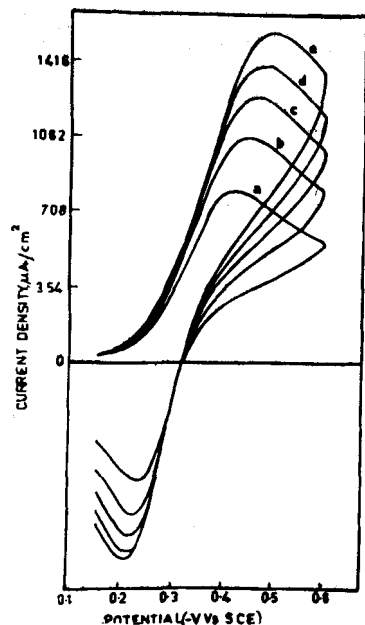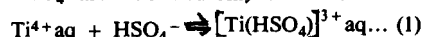
Fig. 4. Cyclic voltammogram of Ti^{+4}- (concentration 10 mM) in 0.2M oxalic acid containing 35 mM H_2SO_4 at sweep rates (a) 20 mV/sec (b) 40 mV/sec (c) 60 mV/sec (d) 80 mV/sec (e) 160 mV/sec

DISCUSSION

Even on Hg electrode, uncomplexed Ti^{4+} in H_2SO_4 is reduced only around —0.900 V when mM concentrations are employed [14-17]. The reduction at lower potentials are noted only when very high Ti^{4+} concentrations [13] or very high SO_4^{2-} concentrations [14] are employed. As discussed before [19,23], this happens because the complex formation between Ti^{4+} and HSO_4^- are facilitated only at such conditions.

$$Ti^{4+}aq + HSO_4^- \rightleftharpoons [Ti(HSO_4)]^{3+}aq... \quad (1)$$

The above behaviour noted on Hg [13-17] and GC [19] is also noted in the present work on Cu electrode. At sufficiently long time scales (low sweep rates) the complex formation goes to completion and the overall response is diffusion-controlled. At shorter time scales (higher sweep rates), the kinetics of formation of the sulphate complex near the electrode surface has an influence on the overall process and hence the $i_p/V^{1/2}$ decreases.

The diffusion-limited peak current constant $i_p/AC_{Ti^{4+}}V^{1/2}$ is found to be approximately a constant for sulphate as well as oxalate complexes. (Table II).

This suggests that the diffusion coefficients of both the complexes are almost equal in both the media (H_2SO_4 and oxalic acid) considered here.

The significant aspect in the present work probably is the fact that on Cu also the charge transfer kinetics of Ti^{4+}/Ti^{3+}-oxalate complex is rather slow when compared with Hg. The CV data on Hg presented earlier [24] indicate that the $k_{h,app}^\bullet$ (Hg) is around 1.2×10^{-1} cm/sec. The $k_{h,app}^\circ$ on Cu can be obtained from the ΔE values of CV curves. For each ΔE value a corresponding ψ value has been tabulated [25,26] which is given by

$$\psi = \frac{(D_{ox}/D_{Red})^{\alpha/2} \cdot k_h^\circ}{(D_{ox}.\pi.n.F.v/RT)^{1/2}}$$

Table II: Voltammetric characteristics of sulphate and oxalate complexes of Ti⁴⁺/Ti³⁺ redox system on Hg, GC, Cu electrodes

System	Electrode material	i_p • AC $V^{1/2}$	$E_{1/2}$ ** Volt vs SCE	K_h° app cm sec⁻¹
Ti⁴⁺-sulphate in H₂SO₄	Hg	—	-0.270 -0.596	—
	GC	453.7	-0.435	—
	Cu	425.4	-0.405	—
Ti⁴⁺-oxalate in oxalic acid	Hg	—	-0.300	1.2×10^{-1}
	GC	451.3	-0.325	1.2×10^{-3}
	Cu	430.4	-0.310	2.9×10^{-3}
Ti⁴⁺ sulphate in oxalic acid containing 35mM H₂SO₄	Hg	—	—	—
	GC	450.7	-0.395	1.1×10^{-4}
	Cu	470.3	-0.375	6.2×10^{-4}

• $= i_p$ in μA, C in mM and V in Volt sec⁻¹
** $= E_{1/2}$ value in LSV curves are taken as equal to $\dfrac{E_p + E_{p/2}}{2}$

In this equation, if we assume that D_{ox}/D_{Red} is approximately one (this is valid in $i_{p,c} \simeq i_{p,a}$ in all cases) we can easily calculate k_h° knowing D_{ox} (8.31×10^{-6} cm²/sec) from the literature [27] and all other constants. Typical calculations for Ti⁴⁺-oxalate in oxalic acid are presented in Table 1. The k_h° (GC) was also calculated earlier. Comparison of the k_h° values on Hg, Cu and GC now indicates that the k_h° value decreases in this order. The k_h° value on GC electrode would generally be lower when compared with metal electrode [22,28]. But a decrease in k_h° on Cu by nearly 40 times when compared with Hg is certainly suprising. It is certainly necessary to reevaluate the thinking that in the case of simple electron-transfer processes all the electrodes would behave in a similar fashion [29].

Much more detailed and extensive experiments are required before the cause of slower charge-transfer kinetics on Cu electrode is understood properly. However, it seems that the difference in the adsorbability of supporting electrolyte anions on Cu and Hg is the major cuase for this behaviour. The decrease in k_h°, app noted on Cu with the addition of smaller amounts of H_2SO_4 and KCl lends support to this view (Table I). It appears that the SO_4^{2-} and Cl^- anions exert an even stronger blocking effect on the electron-transfer kinetics when compared with oxalate anions. On sulphate addition the $k_{h,app}^\circ$ on GC also decreases for the Ti⁴⁺/Ti³⁺-oxalate redox system (Table II). This value is also less than the $k_{h,app}^\circ$ on Cu (Table II) as would be expected [22,28].

Finally, the implication of the present work on the general use of Ti^{4+}/Ti^{3+} redox system for the reduction of aromatic nitro and nitroso compounds [11,12] should also be discussed. These processes show very good efficiency only when very high acid concentrations (H_2SO_4) are employed. The reason for this is quite obvious from the present work. The formation of easily reducible Ti⁴⁺ - sulphate complex is facilitated by the higher acid concentration. The apparent $E^{1/2}$ values of the reduction of Ti⁴⁺ (sulphate complex (-0.405V) is only about 30 mV more negative than the oxalate complex (-0.375) as shown in Table II. Hence it is obvious that in the preparative electrolysis, substantial voltage saving may not be effected even if Ti⁴⁺- oxalate complex is used instead of sulphate complex. However, the Ti³⁺- sulphate species is found to be less stable (no anodic

peak on Cu and a relatively small anodic peak even on OC at much more positive potential region, [19] when compared with Tl^{3+}-oxalate species which is quite stable and gives a well defined reoxidation peak. The reaction rate between these Tl^{3+}- oxalate species and the aromatic nitro and nitroso compound may be different and their influence on the overall reduction efficiency is worth investigating further.

CONCLUSION

The present studies indicate that the sulphate complex of Tl^{4+}-species is much more easily reduced when compared with the uncomplexed species on Cu electrode. In this regard, the behaviour observed here is quite consistent with the earlier studies on Hg and OC electrodes. The charge-transfer rate constant on Cu however is about 40 times lower on Cu when compared to Hg. This significant result showing such a wide difference in rate constants between two metal electrodes themselves is probably associated with the difference in the blocking effects of supporting electrolyte anions. The SO_4^{2-} and Cl- anions seem to exert even greater blocking when compared with oxalate anions. The possible implication of the use of oxalate complexes of Tl^{4+}/Tl^{3+} redox system for the reduction of aromatic nitro and nitroso compounds require further, more careful investigation.

REFERENCES

1. M W Breiter, *Electrochemical Processes in Fuel Cells*, Springer-Verlog, N.York (1969)

2. S Srinivasan, H Wroblova and P O'M Bockris. *Adv Catalysis* 17 (1967)351

3. J P Hoare, *The Electrochemistry of Oxygen*, Wiley-Interscience, N. York (1968)

4. A J Appleby, *Modern Aspects of Electrochemistry*, Vol 9 (B E Conway and J O'M Bockris Ed) Plenum, N. York (1974) 368

5. R W Murray, in *Electroanalytical Chemistry*, Vol.13 (A J Bard Ed) Marcel Dekker, N. York (1983) p 191

6. M Noel, P N Anantharaman and H V K Udupa, *Trans. SAEST*, 15 (1980) 49

7. E M Genies, G Bidan and A F Diaz, *J Electroanal Chem*, 149 (1983) 101

8. G P Kittleson, H S White and M S Wrighton, *J Am Chem Soc*, 106 (1984) 7389

9. R W Adzic, *Advances in Electrochemistry and Electrochemical Engineering*, Vol.13 (H Gerischer Ed) Wiley-Interscience, N. York (1984) p 159

10. S Trasatti and W E O'Grady, *Advances in Electrochemistry and Electrochemical Engineering* ,Vol.12 (H, Gerischer Ed) Wiley Interscience, N. York (1981) p 177

11. M Noel, P N Anantharaman and H V K Udupa, *J Applied Electrochem*, 12 (1982)291

12. M Noel, P N Anantharaman and H V K Udupa, *J Electrochem Soc India*, 32 (1983) 151

13 O Ess, *Acta Physicochem, USSR* 13 (1940) 429

14 G M Habashy, *Collect Czech Chem Commun*, 25 (1960) 3166

15 G M Habashy, *Z Anarg U Allgem Chem*, 306 (1960) 312

16 F G Banica and L Carlie, *Rev Chim*, 30 (1979) 640

17 Ya I Turyan and L M Maluka, *Zh Obsche Khim*, 51 (1981) 273

18 M Noel and P N Anantharaman, *Electrochim Acta* 28 (1983) 477

19 M Noel, P N Anantharaman - sent for publication in *Anal Chim Acta*

20 M Noel, P N Anantharaman and A V K Udupa, *Electrochemicals Bulletin*

21 M Noel and P N Anantharaman, *J Electroanal Chem* 191 (1985) 127

22 M Noel and P N Anantharaman, *The Analyst*, London 110 (1985) 1095

23 M Noel and P N Anantharaman, *Advances in Electrochemicals*, CECRI, Karaikudi, India (1948) p.47

24 J M Saveant and E Vianellao, *Electrochim Acta*, 19 (1965) 905

25 R S Nicholson *Anal Chem* 37 (1965) 135

26 S P Perone *Anal Chem*, 38 (1966) 1158

27 R L Pecsok, *J Am Chem Soc*, 73 (1951) 1304

28 R J Taylor and A A Humffray *J Electroanal Chem*, 42 (1973) 347

29 A Capon and R Parsons, *J Electroanal Chem*, 46 (1973) 215