Cyclic Voltammetric and Chronopotentiometric Studies of Cerium IV Reduction

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Electrode reaction of Ce(IV) - Ce(III) was studied in potassium carbonate medium at hanging mercury drop electrode. The electrode reaction was found to be irreversible but diffusion controlled. The diffusion coefficient of Ce(IV) in this medium was calculated by Sand's equation and found to be equal to 3.65 x 10^{-6} cm^2/sec. The kinetic parameters: α, k_s and k^o_f were found to be 0.85, 1.08 x 10^{-4} cm/sec and 3.9 x 10^{-5} cm/sec respectively.

Voltammetry of cerium has been investigated at graphite [1] and glassy carbon electrodes [2]. Agrawal and Kapoor [3] studied cerium reduction in thiocyanate medium. The potential of the reduction of the ceric to cerous ion is so positive that the diffusion current starts at zero applied e.m.f. The standard potential of the cerous - cerium couple (-1.924 V *vs* S.C.E.) is so negative that the hydrogen reduction interferes with the determination of cerium at mercury electrode. It is found that the carbonate complex of cerium is quite stable. The shift in the peak potential is so negative that it is possible to study the reduction of Ce(IV) at hanging mercury drop electrode.

EXPERIMENTAL

A Beckman Electroscan -30 recording instrument was used in the present work. A three electrode system was required to be used on this instrument. A hanging mercury drop electrode (manufactured by Beckman company), a platinum wire and saturated calomel were used in the present work as indicator, auxiliary and reference electrodes respectively. A tri-dentate electrolysis cell (as reported earlier [4]) was used for this work.

Analytical grade chemicals and doubly distilled water were used in all measurements. Stock solution of cerium was prepared from ceric sulphate of AnalaR grade.

RESULTS AND DISCUSSION

Cyclic Voltammetry

Different concentrations, varying from 0.4 mM to 0.8 mM were taken in 0.8 M K_2CO_3 supporting electrolyte and pH was adjusted to 10.8. Cyclic voltammograms were recorded at a scan rate of 40 mV/sec (Fig.1). Well defined cathodic and anodic peaks were obtained at -0.42 V and -0.28 V *vs* S.C.E. respectively.

For a reversible system $(i_p)_c = (i_p)_a$; separation of these peaks $[(E_p)_c-(E_p)_a = \Delta E_p]$ = 60/n mV. But in the present case Δi_p = 0.7 μA and ΔE_p = 140 mV. This shows that the reduction of Ce(IV) to Ce(III) is irreversible in nature. Current concentration proportionality proves that the reduction is diffusion controlled

The standard rate constant, k_s, is given by [5]

$$\Psi = \frac{v^{\alpha} k_s}{(\pi a D v)^{1/2}}$$

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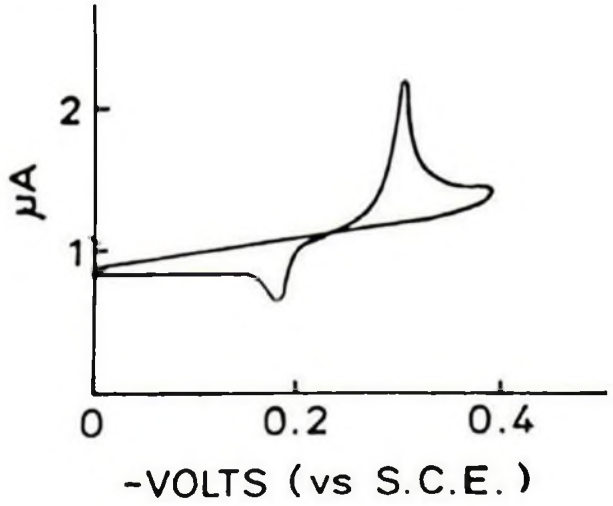


Fig.1 Cyclic Voltammograms of 0.6 mM Ce in K_2CO_3 medium.

where a = nF/RT; v the scan rate in volt/sec; α is transfer coefficient; $(D_o/D_R)^{1/2}$ is the square root of the ratio of diffusion coefficients. This is almost unity .

The exact variation of ΔE_p with Ψ is reported in literature [5]. (For ΔE_p = 140 mV, Ψ =0.255). From the value of Ψ thus obtained, the k_s (standard rate constant) value is calculated and found to be 1.08 x 10^{-4} cm/sec., indicating the quasi-reversible nature of the electrode reaction.

Current reversal chronopotentiometry

The $E_{\tau/4}$ for Ce(IV) reduction in potassium carbonate supporting electrolyte is -0.38 V. For the reversal chronopotentiogram, the transition time of the reverse step (τ) was so small that $(E_{\tau/4})_a$ was not measurable (Fig.2). This indicates that the rate of charge transfer process is slow. Diffusion coefficient of Ce(IV) in potassium carbonate, calculated by Sand's equation, is found to be 3.65 x 10^{-6} cm^2/sec.

The potential-time equation for irreversible reaction is [6]

$$E = E^\circ - RT/nF \ln (nFAC_a k_a/I) + RT/\alpha nF \ln [\tau^{1/2} - t^{1/2} / \tau^{1/2}] \quad ..(2)$$

A plot of decimal logaritham of $[1-(t/\tau)^{1/2}]$ *vs* potential is a straight line

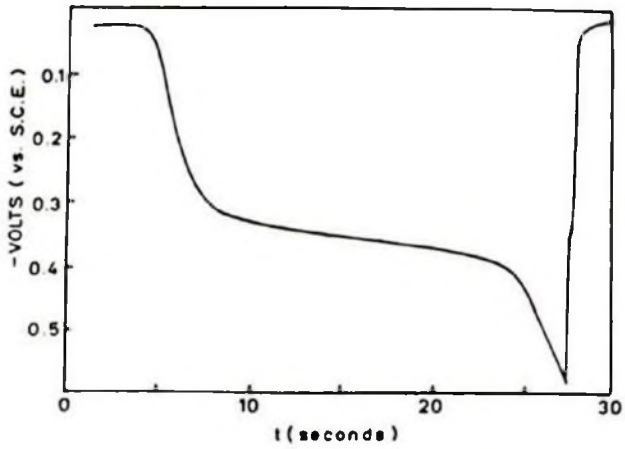


Fig.2 Current - reversal Chronopotentiogram of 0.8 mM Ce in K_2CO_3.

(Fig.3) whose slope is 2.303 RT/αnF. From the experimental slope, α was found to be 0.85. The forward rate constant k°_f calculated from the equation (2) is 3.0 x 10^{-5} cm/sec.

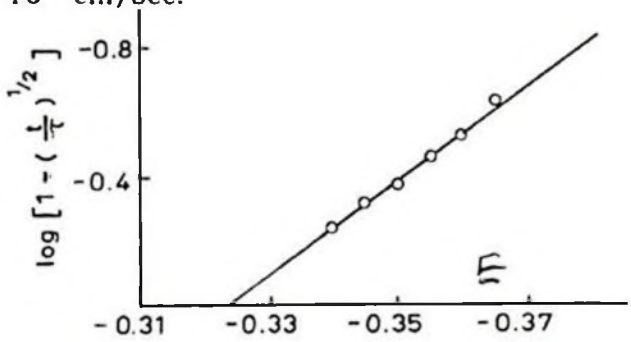


Fig.3 A plot of log $[1-(t/\tau)^{1/2}]$ *vs* Potential

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