

A study on non-faradaic yields of anodic contact glow discharge electrolysis using cerous ion as the $\text{OH}^\bullet$ scavenger : An estimate of the primary yield of $\text{OH}^\bullet$ radicals

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Chemical yields of contact glow discharge electrolysis (CGDE) show strong deviations from faradaic behaviour. The products are novel for normal electrolysis and yields significantly exceed the Faraday law value. Anodic CGDE gives rise to Ce^{4+} and H_2O_2 in the anolyte in yields significantly exceeding the faradaic value besides the faradaic yield of O_2 . The relative yield of Ce^{4+} and H_2O_2 depends on the concentration of Ce^{3+} and the quantity of electricity passed. A kinetic analysis of the variation of the initial differential yield of Ce^{4+} , $G_0(\text{Ce}^{4+})$ with the concentration of Ce^{3+} after applying certain approximations leads to an estimate of the generation of 12 moles of $\text{OH}^\bullet$ radicals in the liquid phase reaction zone of anodic CGDE for the passage of each mol electron of electricity.

In contact glow discharge electrolysis (CGDE) a plasma is sustained by dc glow-discharges between an electrode and the electrolyte around it. Conventional electrolysis switches spontaneously over to full CGDE when the voltage applied reaches a threshold value, the mid-point voltage (V_D)¹⁻³. Highly remarkable are the chemical effects of CGDE. The products are novel for conventional electrolysis and in yields several times the Faraday law value^{1, 2, 4, 9}. The non-faradaic yields of anodic CGDE of inert-type aqueous electrolytes comprising H_2 , H_2O_2 and O_2^E (O_2 in excess of the faradaic yield) originate in two reaction zones⁸: the liquid phase near the plasma-anolyte interface where sufficiently energised gaseous H_2O^+ ions from the plasma break up the liquid water molecules on collision into $\text{H}^\bullet$ and $\text{OH}^\bullet$ radicals¹⁰ which trigger off further reactions giving rise to

H_2O_2 and the majority of the yields of H_2 and O_2^E and the plasma round the anode where a part of H_2 and O_2^E are produced by dissociation of water vapour in glow discharges. Anodic CGDE is thus a potential technique for generating radicals in a liquid at a high local concentration. This is substantiated by conversion of aqueous formic acid into oxalic acid⁹, and of liquid ammonia into hydrazine⁴ both in yields several times the Faraday law value. It is thus of interest to study systematically the chemical effects from the liquid phase reaction zone of anodic CGDE in the presence of potential $\text{OH}^\bullet$ radical scavengers. Herein are discussed the results for Ce^{3+} , a scavenger.

Experimental

Chemical effects of anodic CGDE of Ce^{3+} solutions were studied using a H-type Corning cell fitted with a G-5 glass sinter dividing the electrode compartments and having facilities for collecting electrolysed solutions as well as electrode gases from each compartment as described in an earlier report⁸. Power was supplied at 450 V (when anodic CGDE generates in full form just switching on the power^{3, 8, 9} and at current densities $900 \pm 50 \text{ mA cm}^{-2}$. The quantities of electricity passed were upto 25 C. The following standard conditions were employed for the study: anolyte, 0.5 M H_2SO_4 plus varying concentrations (0.02 M - 0.12 M) of $\text{Ce}_2(\text{SO}_4)_3$; catholyte, 0.02 M H_2SO_4 plus 0.05 M K_2SO_4 ; anolyte and catholyte were pre-boiled and degassed; anode, Pt wire of length 5 mm and diameter 0.35 mm; cathode, 1 cm² Pt foil of thickness 0.20 mm; ambient temperature, $85 \pm 2^\circ\text{C}$; and pressure, atmospheric. Current was supplied from an Aplab 7322 medium voltage d c power supply which provided a maximum of 1.5 A at voltages upto 600 V. Quantity of electricity passed during anodic CGDE was measured on a precalibrated ESC 640 digital coulometer.

The yields produced in the anolyte comprised H_2O_2 and Ce^{4+} , their relative amounts depending on

the number of coulombs passed and the concentrations of Ce^{3+} . H_2O_2 in the anolyte was determined by titrating a 20.0 ml aliquot with standardised $4.4 \times 10^{-4} \text{ M}$ KMnO_4 acidified with 2 M H_2SO_4 . The Ce^{4+} content was estimated by the addition of a known excess of $1.25 \times 10^{-3} \text{ M}$ H_2O_2 to a 20.0 ml aliquot followed by titration of the remaining H_2O_2 with acidified $4.4 \times 10^{-4} \text{ M}$ KMnO_4 solution (no interference from Ce^{3+} could be detected with standard Ce^{4+} solution). A satisfactory material balance was observed among Ce^{4+} , H_2O_2 and O_2^{E} , and H_2 produced at the glow discharge anode.

Results and discussion

Ce^{4+} and H_2O_2 formed in the anolyte during anodic CGDE of Ce^{3+} solutions interact mutually to yield Ce^{3+} back and O_2 . The relative yield of the two products was found to depend on both the concentration of Ce^{3+} and the quantity of electricity (q) passed. Further no net formation of Ce^{4+} when $[\text{Ce}^{3+}] < 0.02 \text{ M}$ and H_2O_2 when $[\text{Ce}^{3+}] \geq 0.04 \text{ M}$ could be observed. The yield of H_2O_2 increased with q approaching a limiting value for $[\text{Ce}^{3+}] \leq 0.02 \text{ M}$ but decreased at higher $[\text{Ce}^{3+}]$. On the other hand the yield of Ce^{4+} only increased with q approaching a limiting value.

A useful way of expressing the yield of a product (X) of CGDE is by quoting its G_0 -value, a dimensionless quantity^{1,8} defined as:

$$G_0(\text{X}) = \frac{\text{Initial differential yield of X (mol per mol electron)}}{\text{Faradaic yield of X (mol per mol electron)}}$$

in analogy with G -value for the yield (molecules per 100 eV) in radiation chemistry, the initial differential yield being the slope of the tangent at the origin of the yield vs. q curve. The values obtained for $G_0(\text{Ce}^{4+})$ and $G_0(\text{H}_2\text{O}_2)$ at different $[\text{Ce}^{3+}]$ (Table 1) show clearly that anodic CGDE gives rise to several times the faradaic yield for Ce^{4+} and H_2O_2 . Further, $G_0(\text{H}_2\text{O}_2)$ fell with $[\text{Ce}^{3+}]$ reaching zero at $\sim 0.03 \text{ M}$ Ce^{3+} where $G_0(\text{Ce}^{4+})$ commenced and rose with further increase in $[\text{Ce}^{3+}]$ approaching finally a limiting value, indicating the occurrence of other reactions competing kinetically with the oxidation of Ce^{3+} during anodic CGDE. In the region of low $[\text{Ce}^{3+}]$, H_2O_2 formation is

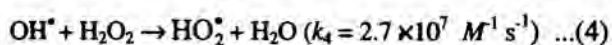
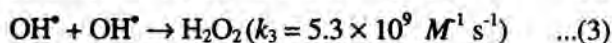
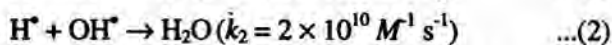
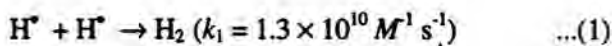
predominant and no Ce^{4+} could be detected. However, at higher $[\text{Ce}^{3+}]$, Ce^{4+} formation dominates over H_2O_2 formation showing a more effective kinetic competition of a Ce^{3+} with an $\text{OH}^{\bullet}$ for another $\text{OH}^{\bullet}$, the precursor for H_2O_2 .

During anodic CGDE highly energised gaseous H_2O^+ ions from the plasma bombard liquid H_2O molecules at the plasma-anolyte interface to break them up into $\text{H}^{\bullet}$ and $\text{OH}^{\bullet}$ radicals which mutually interact to yield H_2 , H_2O_2 and O_2^{E} in accordance

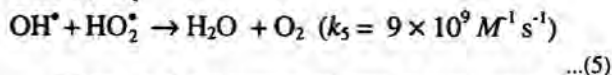
Table 1- Variation of $G_0(\text{H}_2\text{O}_2)$ and $G_0(\text{Ce}^{4+})$ with concentration of Ce^{3+} during anodic CGD of cerous sulphate solutions.

$[\text{Ce}^{3+}]$ (M)	$G_0(\text{H}_2\text{O}_2)$	$G_0(\text{Ce}^{4+})$
Nil	3.6	Nil
0.02	1.9	Nil
0.03	-0.2	0.2
0.04	Nil	1.1
0.06	Nil	1.8
0.08	Nil	2.5
0.10	Nil	3.0
0.12	Nil	3.3

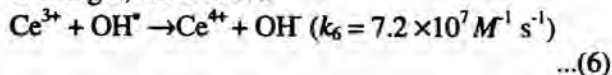
with Hickling's radiolytic mechanism¹ (the rate constant values quoted are from pulse radiolysis data¹¹):



followed by



Thus, in the absence of any radical scavenger, $G_0(\text{H}_2\text{O}_2)$ would measure the total non-faradaic yield from the liquid phase reaction zone. However in the presence of Ce^{3+} , a potent $\text{OH}^{\bullet}$ radical scavenger, the reaction



would compete kinetically with the reactions (2) and (3). Further Ce^{4+} would undergo reduction by

H₂O₂ into Ce³⁺ and O₂. Applying the principle of competition kinetics, an expression for $G_0(\text{Ce}^{4+})$ is obtained:

$$G_0(\text{Ce}^{4+}) = n \frac{[\text{Ce}^{3+}] - A}{[\text{Ce}^{3+}] + A + B} \quad \dots(7)$$

where, n is the number of moles of OH[•] radicals produced for the passage of one mol electron of electricity, A and B stand for $\frac{k_3}{k_6} [\text{OH}^*]$ and $\frac{k_2}{k_6} [\text{H}^*]$

respectively. The expression predicts an upward trend for $G_0(\text{Ce}^{4+})$ with $[\text{Ce}^{3+}]$ towards a limiting value as observed (Table 1). The same considerations predict a downward trend (Table 1) in $G_0(\text{H}_2\text{O}_2)$ with $[\text{Ce}^{3+}]$:

$$G_0(\text{H}_2\text{O}_2) = n \frac{A - [\text{Ce}^{3+}]}{[\text{Ce}^{3+}] + A + B} \quad \dots(8)$$

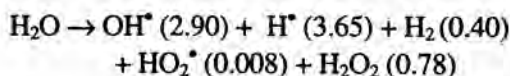
The concentration of the radicals will change as these advance into the bulk anolyte. The kinetic situation in the liquid phase reaction zone of the anodic CGDE is thus highly complex and requires a complete knowledge of concentration profiles of all the reactant species over the reaction zone for its solution. However, the application of a crude approximation where A and B can be considered as constants, justifiably for species like Ce³⁺, the rate constant for the reaction of which with OH[•] radicals is low enough ($k_6 = 7.2 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$), leads to the expression^{1,12} (9)

$$\frac{1}{G_0(\text{Ce}^{4+})} = \frac{1}{n} + \frac{1}{n} \frac{2A + B}{[\text{Ce}^{3+}] - A} \quad \dots(9)$$

The plot $\frac{1}{G_0(\text{Ce}^{4+})}$ versus $\frac{1}{[\text{Ce}^{3+}]}$ at large

enough $[\text{Ce}^{3+}]$ was found linear as predicated by Eq. (9). From the intercept of the plot, the number of moles of OH[•] radicals (' n ') generated by 1 mol electron of electricity was estimated to be 12.8. This agrees fairly well with the ' n ' value of 8 estimated from anodic glow discharge electrolyses (GDE where the anode is placed in the gas space above the anolyte surface) of Ce³⁺ solutions^{1,12} indicating significant similarity between the mechanism operating in the liquid-phase reaction

zone of anodic CGDE and the one in anodic GDE. Further, there exists a strong analogy between the chemical effects of anodic CGDE and those of radiolysis of aqueous solutions. It is thus worth comparing the yield of radicals from the two processes. Radiolysis of water ($\text{pH} = 0.46$) by γ -rays or fast electrons with energies in the range 0.1 - 20 MeV produces the following yields in molecules per 100 eV^{11,13},



This implies a maximum yield 4.5 moles for OH[•] radicals per mol electron of electricity if the H₂O_{gas}⁺ have average energies of 100 eV as against the yield of more than 12 moles per mol electron of electricity by anodic CGDE. Thus it appears that during anodic CGDE the average energy of the positive gaseous ions entering into the liquid anolyte from the plasma over the anode is appreciably greater than 100 eV.

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