Water Oxidation to Oxygen by Cerium(IV) Ions mediated by Ruthenium Dioxide Catalyst

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Cerium(IV) ions are shown to oxidize water to O_2 in the presence of RuO_2 catalyst in 0.5 mol dm^{-3} H_2SO_4 solution. The yield of oxygen depends strongly on the relative concentrations of Ce^{4+} and RuO_2. High ratios of Ce^{4+} to RuO_2 favour corrosion of the catalyst, a fact which is explained by electrochemical concepts. Our results are discussed in relation to an earlier proposition concerning the mechanism of the water oxidation reaction by Ce^{4+} ions in this system.

A recent publication by Mills[1] concerning the reaction of Ce^{IV} with water in the presence of RuO_2 [equation (1)]

$$4Ce^{4+} + 2H_2O \xrightarrow{RuO_2} 4Ce^{3+} + 4H^+ + O_2 \quad (1)$$

prompts us to report our own observations regarding this process. The present findings substantiate previously published data.[2]

Experimental

Experiments were performed at room temperature with solutions of cerium(IV) sulphate (BDH) in 1N H_2SO_4. Hydrated ruthenium dioxide (Alpha Inorganic) was employed throughout the work. The catalyst was added to the cerium(IV) solutions previously flushed with nitrogen to remove O_2. Oxygen analysis was carried out for a reaction time of 30 min during which the solution was stirred. In a first series of experiments performed at the Royal Institution, O_2 was determined polarographically as previously described by Harriman and Mills.[3] Ruthenium tetroxide was extracted from the reaction mixture with CCl_4 (10 cm^3) and analyzed photometrically according to Connick and Hurley[4] (ε at 310 nm = 2 500 dm^3 mol^{-1} cm^{-1}).

In a second series of experiments performed at the Ecole Polytechnique Lausanne the detection system used for O_2 analysis was an END-O-MESS apparatus.[2] A trap maintained at −70 °C was placed in between the solution flask and the detection unit. This removes water and RuO_4 from the nitrogen used as carrier gas. Experimental results obtained with the two methods were in good agreement.

Results

The Table lists the amount of oxygen generated from the oxidation of water by cerium(IV) in the presence of $RuO_2 \cdot xH_2O$ redox catalyst under various experimental conditions. This is expressed as % yield expected from the stoicheiometry of equation (1) [and based on the initial concentration of cerium(IV)]. (It is assumed that the reaction proceeds to completion.) Consider first the results obtained at 3.5×10^{-3} mol dm^{-3} initial cerium(IV). The yield of O_2 increases from 40% at 0.5 mg $RuO_2 \cdot xH_2O$ to 63% at 50 mg catalyst in the same reaction volume. Heat treatment changes the efficiency of the catalyst (1.2 mg per 30 cm^3 solution), yielding 67% O_2 when pretreated in air for 5 h at 140 °C and 30% O_2 at 400 °C. Furthermore, the concentration of cerium(IV) ions present initially in solution also affects the oxygen yield since the latter increases from 60 to 73% when [Ce^{4+}] is lowered from 3.6×10^{-3} to 1.8×10^{-3} mol dm^{-3}. It should be emphasized that these results are the averages from several measurements and were reproducibly obtained in the two laboratories.

Discussion

Our experimental observations can be rationalized in terms of electrochemical arguments. The redox potential of the Ce^{4+} ion-containing solution is given by equation (2) (T = 298 K),

$$E(\text{n.h.e.}) = 1.45 + 0.059 \log([Ce^{4+}]/[Ce^{3+}]) \quad (2)$$

while the standard electrode potentials of the H_2O–O_2 and RuO_2–RuO_4 couples are located at 1.23 and 1.4 V, respectively. The fact that RuO_2 corrodes to RuO_4 in acid solution under high anodic bias is known from electrocatalytic studies with acid–water electrolyzers.[5] Corrosion sets in at electrode potentials more positive than 1.4 V and can be prevented by replacing RuO_2 with IrO_2[6,*] or using mixtures of both oxides. The conditions encountered by an RuO_2 particle in a Ce^{4+}-containing solution are comparable to those of an electrocatalyst under anodic bias. The electrochemical potential of the particle will depend on the rates of water (and RuO_2) oxidation and that of Ce^{4+} reduction and is situated somewhere between that of the $Ce^{4+/3+}$ redox couple and 1.23 V. The higher the initial Ce^{4+} concentration and the lower the amount of RuO_2 catalyst the more positive will be the electrochemical potential of the RuO_2 particle and the more likely its fate will be corrosion to RuO_4.

From these considerations one would predict that the oxygen yield should decrease with increasing Ce^{4+} and decreasing $RuO_2 \cdot xH_2O$ concentrations. In agreement with this expectation is the experimental observation (Table) that the O_2 yields are lowest for high Ce^{4+} : RuO_2 ratios, where corrosion of the particle occurs at the expense of water oxidation. High-temperature treatment inactivates RuO_2 catalysts,[5] decreasing the rate of water oxidation. Such an effect should favour RuO_4 formation since it produces a positive shift of the mixed potential of the particle under identical conditions of Ce^{4+} and RuO_2 concentration. Again, experimental results confirm this prediction.

A direct comparison of our data with those published by Mills[1] is difficult since he refrained from presenting quantitative results on the amount of O_2 produced in the oxidation of water by Ce^{4+}. Even with respect to RuO_4, claimed to be a major reaction product, only qualitative analysis (smell, colour) was performed. Other spectroscopic results presented in ref. 1 refer to hypothetical intermediates from the decompo-

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[*] In our initial report we used PtO_2 or IrO_2 as redox catalyst, *not* RuO_2 as implied by Mills.[1]

Table. Oxygen yields from the reaction of Ce^{4+} with water in 1N H_2SO_4 in the presence of $RuO_2 \cdot xH_2O$; reaction volume 30 cm^3

$RuO_2 \cdot xH_2O$ (mg per 30 cm^3)	0.6[a]	5	10	20	35	50	1.2						20[b]
θ_c[c]/°C	25						140	200	250	300	370	400	25
$10^3[Ce^{4+}]$/mol dm^{-3}	3.6[a]												1.8[b]
O_2 yield (%)	40	48	60	60	62	63	67	66	62	55	40	30	73

[a] Conditions as in ref. 1. [b] Conditions as in ref. 2. [c] Temperature of pretreatment of the RuO_2 catalyst (5 h in air).

sition of RuO_4 in neutral or basic solution and hence are irrelevant for the problem under study.

One fact which should be stressed when comparing Mills' to our original results[2] is that the concentration ratio of Ce^{4+} to RuO_2 catalyst he used is much higher (*ca.* 68 times) than that employed in our earlier study.[2] A simple calculation shows that this should greatly favour the RuO_2 corrosion over the water oxidation reaction. The $RuO_2 \cdot xH_2O$ employed has a specific surface area of 0.6 m^2 g^{-1} which at the concentration used by Mills (20 mg catalyst per l) represents a total catalytic surface of 120 cm^2 l^{-1}. From the specific capacity of hydrated RuO_2, 142 μF cm^{-2},[7] this surface has a capacity of 1.7×10^{-2} F. Therefore, in order to shift the potential of the RuO_2 particles by 1 V a charge of 1.7×10^{-2} C dm^{-3} is required corresponding to the discharge of only 1.76×10^{-7} mol dm^{-3} Ce^{4+} ions. Such a shift should be sufficient for a RuO_2 particle to reach the (limiting) Nernst potential which is calculated as +1.7 V from equation (2) using the Ce^{4+} concentration employed by Mills (3.6×10^{-3} mol dm^{-3}). This potential lies far above the corrosion onset of RuO_2 and would lead to rapid destruction of the catalyst. A similar calculation shows that for the conditions employed in our earlier studies, *i.e.* 660 mg RuO_2 per l and $[Ce^{4+}] = 1.8 \times 10^{-3}$ mol dm^{-3}, a 38-times larger amount of Ce^{4+} has to be discharged to produce a 1-V shift in the potential of the RuO_2 particles and that the limiting Nernst potential is +100 mV less positive than in Mills' case. From these considerations, it would appear that by using a large catalytic surface area and avoiding high initial oxidant concentration, corrosion of the RuO_2 should be inhibited as is shown by the data presented in the Table. Further confirmation for the validity of this concept comes from work with TiO_2-supported RuO_2 catalysts which we have introduced in water-cleavage systems.[8,9] These are distinguished by a particularly large surface area and as has been shown by Mills[1] are much less susceptible to corrosion than powdered RuO_2.

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