

Electrochemical reduction and oxidation of nitrogen through low-current electrolysis

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MS received 14 June 1976; revised 7 September 1976

ABSTRACT

Dissolved nitrogen is reduced to ammonia at a platinum cathode enclosed in a cellophane membrane and is oxidised to nitric acid at a similarly enclosed anode at very low current density ($\sim 1 \text{ mA/cm}^2$), the electrolyte being distilled water. This is attributed to highly active reducing and oxidising species formed near the cathode and anode respectively under such low-current low-concentration condition of electrolysis.

1. INTRODUCTION

THE author has earlier reported^{1,2} that if electrolysis is conducted at very low current density and/or low concentration a number of anomalous features occur and he has proposed to call it non-Faradaic electrolysis. It is believed^{2,3} that negative charges build up near the cathode and positive charges near the anode and their direct transport or charge leakage is responsible for these anomalies, particularly liberation of an explosive hydrogen-oxygen mixture both at the cathode and at the anode. Since negative charge implies reducing activity and positive charge oxidising activity, it seems likely that the dissolved nitrogen may be reduced at cathode and oxidised at anode. The present paper reports a simple experimental verification of the above idea.

2. EXPERIMENTAL

The experimental set-up is shown in figure 1 (minus *B* and its membrane). This is simply electrolysis of water with platinum foil electrodes with one of the electrodes being enclosed inside a cellophane membrane (well washed with warm acid and later water). The electrolyte is normally distilled water. The electrolysis is allowed to run undisturbed at about 1 mA (about 250 volts D.C. would be necessary).

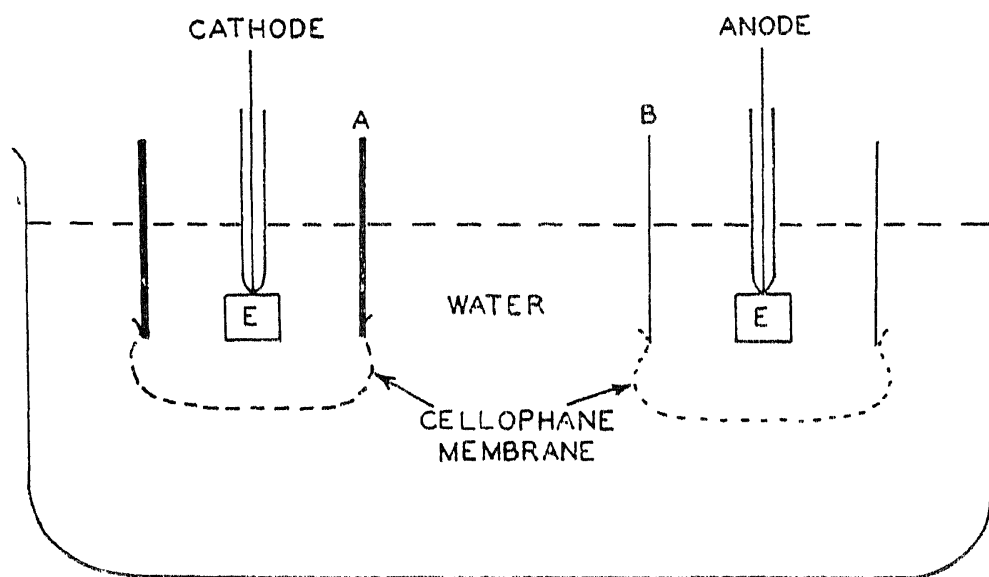


Figure 1. Experimental set-up of the electrolysis cell (A and B: Glass tube supporting the cellophane membrane; E: Platinum foil electrodes).

If the enclosed electrode is the cathode the cathodic solution becomes alkaline to phenolphthalein in a few hours. The cathode solution by overnight electrolysis gives positive test for ammonia (Nessler reagent). The cathode solution on slight acidification with dilute H₂SO₄ and evaporation to a small volume gives strong test for ammonia.

When the enclosed electrode is made the anode (*i.e.*, B exists but not A), the anode solution becomes acidic (pH ~ 3.2) and gives a titration curve characteristic of a strong acid. The solution on evaporation to a small volume after neutralisation gives strong positive test for nitrate (reduction to nitrite followed by diazo colour reaction). Blank tests are to be carried out in both the cases to ensure that the reactions are not due to chance contamination.

Instead of a single compartment as described above a cell with two such membrane regions (as shown in full in figure 1) has also been used with success; this gives simultaneously ammonia and nitric acid respectively in the cathode and the anode chamber. Evidently, the dissolved nitrogen from air is being fixed as ammonia and nitric acid.

We have also successfully used other membranes such as high grade filter paper, fine teflon filter cloth, or porous polyethylene film, but cellophane appears to be the most efficient. The concentration of ammonia and nitric acid produced inside the electrode compartments is somewhat less than N/1000 but increases perceptibly in presence of very dilute acid in the case of ammonia. No ammonia or nitric acid is obtained if the experiment is conducted in a nitrogen-free atmosphere. Also, increasing concentration and/or current strength usually goes against the fixation.

3. THEORY

As already mentioned a considerable quantity of hydrogen gets liberated at the anode under such low-current electrolysis conditions.^{2,3} It has been suggested that this may be due to the formation of H^- or H_2^- or H_2O^- near the cathode ($\text{H} + e = \text{H}^-$; etc.) owing to paucity of current carriers and subsequent migration of these anions to the anode. It is suggested that these reducing species formed near the cathode being exceptionally strong reducing agents reduce the dissolved nitrogen present to ammonia. Similarly, highly oxidising species, probably H_2O^+ or O_2^+ or similar ions, form near anode ($\text{H}_2\text{O} = \text{H}_2\text{O}^+ + e$) and migrate to the cathode to produce co-liberation of oxygen there. These oxidising species oxidise the dissolved nitrogen to nitric acid.

ACKNOWLEDGEMENTS

Thanks are due to Dr. Susanta Sengupta for helpful discussion and Sri Sachi Dulal Sinha and Sri Prithwis Kumar Basu for essential experimental assistance.

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