Letters to the Editor

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ELECTRODE GLOW DURING ELECTROLYSIS AND LIBERATION OF HYDROGEN AND OXYGEN TOGETHER ON THE ELECTRODES

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(*Received December*, 30, 1967)

In a preliminary note (Palit, 1967) the author has reported that on applying a D.C. voltage of about 200 volts, one of the electrodes usually the cathode starts glowing after an initial incubation period. This is accompanied by a sharp drop in current strength, and by the discharge of big bubbles in place of the usual stream of fine bubbles of gas on the glowing electrode as also to some extent on the other electrode. However, the gas liberated on the electrodes on analysis showed results which are novel, unexpected and hitherto unknown, and the present note makes a preliminary report of the same.

Analysis of the Gas—The gas liberated on the cathode on analysis was found to contain both hydrogen and oxygen. However, the oxygen content was not constant. Sometimes the gas cllected over the cathode could be exploded leaving a small residue and at other times the gas could not be exploded by electric spark. The gas collected over various electrolytes (0.2N solutions of hydrochloric acid, ammonium sulphate, barium chloride and potassium chloride) was found to contain on analysis in a Hempel pipette a considerable quantity of oxygen (15 to 50 percent by volume). This is probably the first time that oxygen is reported to be liberated in considerable quantiy at the cathode side. We also checked up the composition of the gas liberated on the non-glowing anode. It was observed that as long as the glow does not start on the cathode, the anodic gas is composed of oxygen only. However, when the cathode starts glowing the gas liberated on

the anode is a mixture of oxygen with a large percentage of hydrogen. Similar things (i.e. the presence of oxygen in the cathodic gas and hydrogen in the anodic gas) are observed even under incipient glow condition, *i.e.* when there is no glow but big bubbles start forming on the respective electrode in place of the usual fine bubles.

Faraday's Law—We checked up to see the relationship between the extent of electrodecomposition and Faraday's law. A number of electrolytes were examined and the results were quite surprising. The volume and composition of the gas liberated by electrodecomposition with the same quantity of electricity was found to be highly variable with the nature of the electrolyte and was usually in excess of that given by Faraday's law. However, the reproducibility was poor, there being large variation in yield from experiment to experiment under apparently the same conditions. Evidently, Faraday's law has nothing to do with this reported phenomenon and the mechanism must be different from normal ionic conduction mechanism.

Mechanism—It is difficult from such preliminary information to venture a suggestion about the mechanism of the observation in question. It was first thought that along with usual electrolysis another concurrent decomposition of water was taking place either due to the catalytic decomposition of water vapour on the glowing electrode, or due to localised high potential gradient owing to microcavity formation, or due to some local action. This idea agreed quite well with observations on barium chloride solution which gives this glow very well and where the volume of oxygen liberated at the cathode side is below 20 per cent. However, in some other cases (HCl, NaOH and KCl) this idea is untenable as the oxygen content of the cathodic gas is between 40 to 50 per cent. Plain decomposition of water can not account for more than one-third volume of oxygen. Besides, the idea of catalytic thermal decomposition of water can not be supported on thermodynamic grounds. The sudden drop of current along with disappearance of turbulence at the onset or near-onset of glow is very significant and is analogous to somedischarge and glow phenomena in gases. Probably some kind of explanation from that field has to be invoked. However, it appears that some ion radicals (probably charged molecular aggregates of water) are involved. This is inferred from the fact that the intensity of glow as well as current strength decreases on applying a magnetic field at right angles to the flow of current. Further experiments are in progress and detailed results will be published later.

Thanks are due to Prithwis Kumar Basu for experimental assistance.

REFERENCE

Palit, S. R., 1967, *Indian J. Phys.* **41** 309.