# Electrolytic decomposition characteristics of ammonia to nitrogen at $IrO_2$ anode

Kwang-Wook Kim[+], Young-Jun Kim, In-Tae Kim, Geun-Il Park, Eil-Hee Lee

Korea Atomic Energy Research Institute
150 Dukjin, Yusong, Daejeon, 305-600, Korea
[+] nkwkim@kaeri.re.kr

## Introduction

Ammonia in wastewater is detrimental to environment in several aspects. The regulations on discharged amount of total nitrogen have become strict. Electrochemical way to decompose the nitrogen compounds to harmless nitrogen gas has attracted a great attention. However, The literature on electrolytic decomposition of ammonia is scant, as compared to other nitrogen compounds, especially on that by the catalytic oxide electrode such as $IrO_2$[1]. In order to understand correctly the decomposition characteristics of ammonia to harmless nitrogen, this work has studied characteristics of adsorption and electrolytic reaction of ammonia at $IrO_2$ anode with a change of pH, and has evaluated decomposition rate to nitrogen, change of byproducts, and effect of chloride ion on the decomposition reaction.

## Experimental

A cell of 24 ml with a cation exchange membrane (Nafion 424), and $IrO_2$ electrode (2cm x 4cm x 0.2 cm) as an anode and etched Ti as a cathode was used with total ammonia solution of 75 ml being circulated. The gases generated from anodic and cathodic chambers and the byproduct ions produced by the electrolytic reaction were analyzed by a GC and IC, respectively. Voltammograms in several conditions were measured to evaluate the electrolytic reaction of ammonia at the electrode with pH. From the measurement of ESR spectra of DMPO-OH adduct through spin-trapping of OH radical, the OH radical generated at the electrode was identified.

## Results and discussion

Figure 1 shows the changes of ammonia and byproduct ions in the solution, and the evolution rates of nitrogen in anodic and cathodic chambers at pH 7 and pH 12. Ammonia existing in pH 12 solution was decomposed mainly to nitrogen gas without oxygen evolution and was slightly converted even to nitrate ion. In the pH 7 solution, where the ammonia exists as a form of ammonium ion, the evolution rate of nitrogen gas much lowered with lots of oxygen evolution. Figure 2 shows voltammograms of ammonia solution at several pH. Taking into consideration of these results, ammonia existing above pH 10 is considered to be first adsorbed at the electrode before conversion to nitrogen. The oxidation of ammonium ion to nitrogen below pH 7 is considered to be due to the oxidation by OH radicals identified by ESR spectra at pH 7, as shown in Fig.3 where the typical spectra of DMPO-OH adduct ESR with peaks of 1:2:2:1[2,3], which was not detected at pH 12. The effect of chloride ion on the decomposition of ammonia was experimentally tested in several ways. On the basis of all results in this work, the decomposition mechanism of ammonia and ammonium ion was suggested as Fig.4.

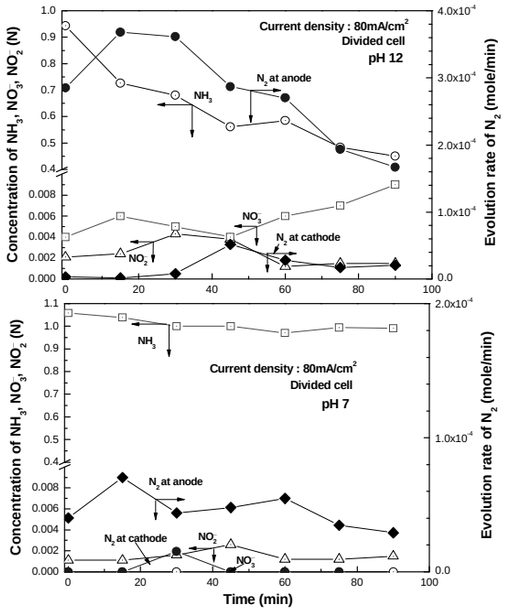


Fig.1 Changes of concentrations of $NH_3$, $NO_3^-$, $NO_2^-$, and evolution rates of $N_2$ in anodic and cathodic chambers of a divided electrolytic cell of Ti-$IrO_2$ with electrolysis time at pH 7 and pH 12

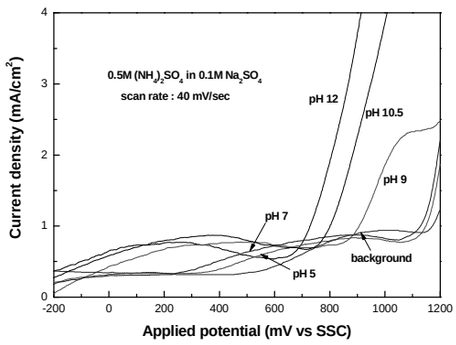


Fig.2 Voltammograms of 0.5 M $(NH_4)_2SO_4$ in 0.1 M $Na_2SO_4$ at $IrO_2$ electrode at several pH.

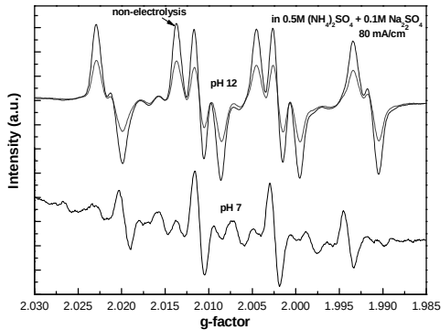


Fig.3 Electron spin resonance spectra of DMPO-OH radical adduct during electrolysis of 0.5 M $(NH_4)_2SO_4$ in 0.1 M $Na_2SO_4$ at pH 7 and pH 12 with applying 80 mA/cm$^2$.

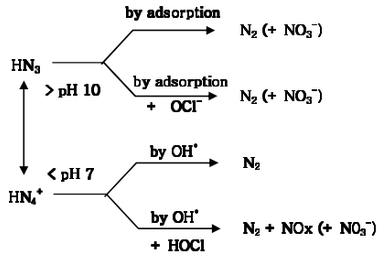


Fig.4 Plausible destruction path of ammonia at an $IrO_2$ electrode.

## References

1. K.-W.Kim, E. H. Lee, et al., Electrochimica Acta, 47(15), (2002) 2524
2. S.Echigo, et al., Wat.Sci.Tech, 34 (1996) 81
3. R.A.Floyd, L.M.Soong, Biochem.Biophy.Res.Commu, 74(1) (1977) 79.