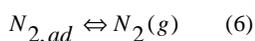
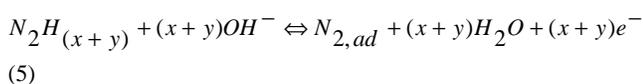
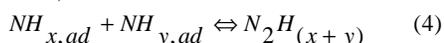
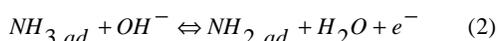


Analysis of Electro-kinetics of Ammonia Oxidation in Alkaline Media by Mathematical Modeling

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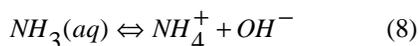
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The study of ammonia electro-oxidation is mainly related with three types of application: 1) fuel cells and fuel reforming (ammonia as a fuel for use in direct fuel cell applications⁽¹⁾ and as a high hydrogen-content fuel for in-situ hydrogen production⁽²⁾), 2) amperometric sensors⁽³⁾ (determination of ammonia content in waters and biological samples), and 3) environmental catalysis (removal of ammonia from contaminated aqueous waste streams). In each application, the prediction and improvement of the kinetics of reaction is critical. The mechanism of ammonia oxidation in alkaline media on platinum substrate has been extensively studied^(4,5,6) since the 60's and more recent investigations^(7,8) tend to confirm the early mechanism suggested by Gerischer⁽⁴⁾:



In this mechanism, step (3) is believed to be rate-limiting,^(4,5,6) step (5) and (6) lead to a sustained production of N₂ whereas step (7) leads to an inactive species N_{ads}, which presumably deactivates the surface by blocking Pt sites. Ammonia adsorption (step (1)) is considered to be fast and to follows Langmuir isotherm.⁽⁴⁾ Under such assumptions, Tafel slopes of 40mV/decade can be predicted, which correspond well with experimental values reported in the literature.^(4,5,6)

More complexity in the determination of the kinetics of reaction arises from the possible coupling with the homogeneous reaction in the bulk:



Ammonium ions are known to be inactive toward adsorption on Pt. In a simulation of ammonia oxidation at ruthenium-titanium oxides planar electrode (diffusion-reaction model) Donten⁽⁹⁾ shows that the experimentally observed increase in the oxidation peak with addition of excess OH⁻ can be reproduced numerically. This shows the importance of considering Equation (8) for a prediction of the overall rate of reaction. However, the author fails to consider Gerischer's mechanism and does not deal with the deactivation of the electrode.

Previous studies on cyclic voltammetry report at low ammonia concentration (10⁻² M and lower) the peak current for ammonia oxidation proportional to the square

root of the sweep rate suggesting a mass-transfer limitation in the rate of reaction^(3,10). Other authors mention that the kinetics order in concentration of ammonia is zero in agreement with a fast adsorption process (step 1).⁽⁴⁾

The objective of this paper is to study electro-kinetics data for the oxidation of ammonia from polarization of a rotating disk electrode using mathematical modeling. Present work focuses on the mechanism on platinum disk. The validity of previously published mechanisms and corresponding limiting step are discussed. A model is proposed and numerically solved that takes into consideration mass transfer at a rotating disk electrode (convection-migration-diffusion), homogeneous reaction of ammonia dissociation, heterogeneous reaction at platinum electrode surface, and possible deactivation of the electrode by N_{ads}. The mass transfer equations at the rotating disk electrode are obtained from Adanuvor and White.⁽¹¹⁾ The speciation of the mixture H₂O-NH₃-KOH is derived following the theory of weak electrolyte as presented elsewhere.⁽¹²⁾ The kinetics of the heterogeneous reaction leading to sustained N₂ production is used as derived by Oswin⁽⁵⁾ and a parallel, slow deactivation reaction leading to N_{ads} accumulation at the surface is included.

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