Mathematical modeling of ammonia electrooxidation kinetics in a Polycrystalline Pt rotating disk electrode

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1. ISE member

Abstract

A mathematical model for the ammonia electrooxidation kinetics, over polycrystalline Pt in alkaline media, was developed through the micro kinetics approach. Two different mechanisms were evaluated for the development of the model, a combined surface-diffusion controlled process and a surface confined process. Nonlinear multiple parameters estimation was implemented by direct comparison with experimental data, obtained in a rotating disk electrode system during linear sweep voltammetry, to calculate the kinetic parameters for the different elementary steps proposed in the mechanisms. It was demonstrated through modeling discrimination techniques that a surface confined process drives the oxidation of ammonia on the implemented electrode surface. The model validates that the formation of N_2 is controlled by the catalytic dimerization of partially reduced ammonia adsorbates (i.e. $NH_{2(ads)}$). Moreover, it confirms that the formation of stronger adsorbed intermediates at high overpotentials is the main cause for the catalyst deactivation.

Keywords: ammonia electrooxidation; ammonia electrolysis; energy storage; hydrogen production; surface confined kinetics.

1. Introduction

The ammonia electrolysis process has proved to be a feasible way for *in-situ* generation of hydrogen, which can be integrated with a fuel cell as an alternative clean power generation source [1, 2]. Among several hydrogen sources, ammonia is identified as one of the most suitable energy carriers since it has a high hydrogen density, it is safer to handle than hydrogen, and there is an available efficient distribution chain [3]. Moreover, fuel grade hydrogen can be produced from ammonia electrolysis with a Faraday's efficiency above 99.9% [4], whilst the ammonia electrolysis potential to treat low ammonia concentration feedstock [5] leads to its application in wastewater treatment along with hydrogen co-generation [6].

In the ammonia electrolysis process, ammonia is oxidized in the anode side of an electrochemical cell to produce N_2 and H_2O while H_2 is evolved from water in the cathode side. This process requires only five percent of the energy used in the water electrolysis for hydrogen production [1, 7, 8]. Although the ammonia electrooxidation reaction has been studied for more than five decades, the mechanism and kinetics involved have not yet been fully established. Therefore, a kinetics model that can be reliably applied in the design and scale up of ammonia electrolyzers needs to be developed.

To date, the most accepted mechanism for ammonia electrooxidation was proposed by Gerischer and Maurer [9]. While most of the experimental evidence supports this mechanism [10-12], it has been difficult to identify the reaction intermediates. This limitation in understanding the nature and role of the intermediates in the reaction mechanism, along with their interactions with the media and catalysts has not yet permitted full development of the ammonia electrooxidation process [13].

Within this context, attempts to understand the ammonia electrooxidation mechanism by means of experimental analysis with different catalysts and support materials have been performed by several researchers [11, 12, 14-21]. However, a comprehensive understanding of the reaction (with postulation of a kinetic rate expression considering the intermediates and the transport and surface phenomena) has not been performed.

In this paper, the micro kinetics model approach was implemented to develop a kinetic rate expression that describes the behavior of ammonia electrooxidation on electrodeposited polycrystalline platinum electrode [22]. A kinetic expression was developed from the mathematical manipulation of the most relevant elementary reactions selected from the literature and the analysis of electrochemical experiments performed in a 0.1 M KOH + 0.01 M NH₄Cl solution. Hence, the model parameters were adjusted against the experimental results and evaluated through the mathematical prediction of the current density in a RDE system subject to linear sweep voltammetry (LSV) perturbations. The mathematical model considered two possible mechanistic approaches: a combined surface-diffusion controlled process (SDCP) and a surface confined process (SCP).

The SDCP mechanism was proposed based on the experimental results presented by Diaz et al. [23], which indicated that the reaction kinetics is strongly affected by the mass transfer of ammonia from the bulk to the electrode surface. Therefore, the SDCP approach accounts for the effect of the mass transfer through an effective diffusivity, while assuming a rate-determining step with the other intermediate reaction steps and adsorbates considered in quasi-equilibrium. On the other hand, the SCP approach accounts for the different surface reaction rates independently.

Both mechanisms were evaluated through modeling discrimination techniques, and a mathematical model that describes the intrinsic kinetics of the ammonia electrooxidation mechanism on polycrystalline platinum electrode was developed.

2. Ammonia electrooxidation

Ammonia in aqueous media can be found either as ammonia ($\text{NH}_{3(\text{aq})}$ in alkaline media) or ammonium (NH_4^+ in acid media). However, the oxidation in acid media has shown to be slow and almost non active [10, 18, 24-26]. Consequently, ammonia is recognized as the active molecule toward electrooxidation. Accordingly, the first proposed mechanisms of the ammonia electrooxidation in liquid phase were approached from its analogue reaction in the gas phase [15, 25].

The first proposed mechanism for ammonia electrooxidation on Pt was developed by Oswin and Salomon [25]. In this mechanism ammonia electrooxidation in alkali media takes place in four consecutive steps (Equations 1-4). Ammonia is initially adsorbed in the active sites (Pt), dissociating to adsorbed NH_2 and H_2O (Eq. 1). The next two steps correspond to consecutive dehydrogenation of $-\text{NH}_2$ and $=\text{NH}$ (Equations 2-3), followed by the association of N_{ads} to form molecular nitrogen.

The analysis of the ammonia electrooxidation kinetic mechanism with Tafel slope, performed by Oswin and Salomon [25], established that the Langmuir isotherm model is the most suitable assumption to describe the adsorption of the intermediates over the active sites. Furthermore, it was concluded that the second transfer reaction and the adsorbed nitrogen association could be the rate determining steps, at low and high currents, respectively.

The second most important mechanism, and to date the most recognized, was developed by Gerischer and Mauerer [9]. In this mechanism the dimerization of partially dehydrogenated adsorbed intermediates NH_x ($x=1,2$), followed by the electrooxidation of the dimerized species, was presented as the most feasible way to get N_2 as main product from the ammonia electrooxidation [10, 11]. The authors utilized ex-situ thermo programmed desorption (TPD) analysis after reaction at potentials higher than 0.6 V vs. reversible hydrogen electrode (RHE) and concluded that the adsorbed atomic nitrogen $N_{(ads)}$ cannot associate to form molecular nitrogen, and therefore becomes a poison for the catalyst. Within this mechanism, it was also considered that adsorbed $OH^-_{(ads)}$ may play an important role in the ammonia electrooxidation mechanism [10]. Equations 5 to 11 describe the Gerischer and Mauerer's Mechanism, where the second electron transfer reaction (Eq. 8), was identified as the r.d.s. [9, 12]. Gerischer and Mauerer's proposed that during the adsorption of the OH^- ions a fraction of the charge (σ) is transferred to the Pt sites where, $0 < \sigma < 1$ [9].

Although, there are no indisputable proofs for the presence of the intermediates proposed by Gerischer and Mauerer, most of the experimental evidence supports its validity [10-13, 15, 19-21, 27-29].

The nature of the reaction intermediates has been analyzed using cyclic voltammetry (CV) in poly crystalline Pt electrodes and differential electrochemical mass spectroscopy (DEMS) [11, 12, 28]. These analyses have confirmed the presence of NH_x species as the main reaction intermediates and the effect of monomolecular adsorbed nitrogen (N_{ads}) as a catalyst poison [12, 15]. Moreover, when the CVs of Pt electrodes in the presence of ammonia were compared with those obtained in ammonia free solutions, some important conclusions were obtained:

- Notwithstanding the CV profiles for ammonia and ammonia free solution in the H_2 under potential deposition region are different, the calculated charge under both profiles showed the same value [11]. De Vooy *et al.* [11] indicated that in the presence of ammonia; this molecule is more preferable adsorbed than water as observed from the

reversible ammonia adsorption peaks A1 and C1 shown in Fig. 1 [12]. Therefore, it can be considered that one atom of ammonia is adsorbed per active site.

- CVs of the Pt electrodes in ammonia solutions (Fig. 1) show that ammonia electrooxidation starts in the double layer region, prior to the region at which the partial oxidation of Pt surface takes place [12, 19, 28]. Additionally, potential-dependent coulometric analysis performed by DeVoy *et al.* [11] concluded that ammonia-kind adsorbates might block the adsorption of OH^- . Therefore, although the presence of OH^- on the surface at the onset potential of ammonia oxidation is not clear [27], it can be assumed that the adsorption of OH^- may not play a relevant role in the ammonia-electrooxidation mechanism to N_2 .
- In reductive CV scans of ammonia electrooxidation, no noticeable reduction peaks can be observed pointing towards the irreversible nature of ammonia electrooxidation to N_2 (which could be caused by catalyst inefficiency and/or blockage of active sites). Just a small cathodic shoulder (peak C2 shown in Fig. 1) attributed to the reduction of adsorbed intermediates back to NH_3 is observed [12, 28].
- Strongly adsorbed nitrogen species can be reduced by operating the electrodes at potentials in or close to the hydrogen adsorption region [26].

Studies in preferentially oriented crystal electrodes, mainly Pt(100) and Pt(111), also showed the ammonia electrooxidation as a surface confined process [19, 21, 30]. A DEMS study performed by Vidal-Iglesias *et al.* [27] on single Pt basal planes demonstrated that the oxidation of ammonia towards N_2 is almost exclusive to Pt(100), while the activity of Pt(111) toward gaseous products is low. Rosca and Koper [10, 19] furthered the kinetic

analysis by calculating the Tafel slopes in single oriented crystal catalysts and concluded that in Pt(111) the r.d.s. is the second electron transfer reaction (Eq. 8), while in Pt(100) the r.d.s. could be the dimerization of NH_2 to form N_2H_4 as in Eq. 9 [21, 30]. Additionally, density functional theory calculations showed that the adsorption energies of different ammonia oxidation intermediates on Pt clusters from lower to higher are -85, -93, -186, -325, and -380 kJ mol^{-1} for $\text{NH}_3 < \text{N}_2\text{H}_4 < \text{NH}_2 < \text{NH} < \text{N}$, respectively [31].

The former conclusions along with the adsorption energies values presented for each one of the feasible ammonia electrooxidation intermediates support the assumption that the pathway to obtain N_2 requires the formation of N_2H_4 and its subsequent electrooxidation, which is recognized to be facile at the potential range where the ammonia electrooxidation takes place [10]. Within this context, it is proposed that the anodic peak attributed to ammonia electrooxidation over polycrystalline Pt in the CV (peak A_2 shown in Fig. 1) is the result of a series of consecutive and parallel reactions, which are described in Eqs. 12 to 17. It must be taken into account that Eq. 14 is not an elementary step, but the sum of all the steps in quasi-equilibrium occurring after NH_2 association.

In a previous work [23], an experimental analysis of the ammonia electrooxidation with RDE coupled with linear sweep voltammetry (LSV) on Pt deposited on Ni electrode in a 0.1 M KOH + 0.01 M NH₄Cl solution was performed. The results showed a linear relationship of the peak potential and the peak current, with the logarithm of the scan rate (ν) and the square root of the scan rate, respectively. This behavior, which was also observed at high rotational speeds led to the conclusion that under the analyzed conditions the mass transfer of NH₃ from the solution bulk to the surface may also play an important role in the reaction rate. An NH₃ effective diffusivity, smaller than the theoretical NH₃ diffusion coefficient, was calculated allowing agreement among experimental data and the theoretical Levich equation [23]. The low value of the effective diffusivity was attributed to possible changes in the local pH within the diffusion layer which could cause ammonia dissociation. However, the validity of this conclusion can be discussed taking into account that this process has been described as a surface confined process [19]. Moreover the presence of adsorbed electro-active species in the LSV experiments can mislead to incorrect interpretations as it is mentioned in the literature [32].

Hereinafter, Eqs. 12 to 17 were used as the base for the development of the mathematical model of ammonia electrooxidation. Experimental data and electrode characterization were collected as presented elsewhere [23].

3. Mathematical model of ammonia electrooxidation

A mathematical model for ammonia electrooxidation in a RDE system under LSV perturbation was developed taking into consideration the following assumptions:

- Kinetics control by rate determining step.
- Langmuir adsorption isotherm for the adsorbed intermediates.
- The RDE is an equipotential electrode and is uniformly accessible.
- Dilute solution theory was used. The aqueous solution is composed by the species NH_3 , OH^- , K^+ , Cl^- , N_2 , and, NH_4^+ .
- Model equations were discretized using the finite difference method.
- Transient state was applied (it was numerically solved by using the implicit method).
- Ammonia electrooxidation follows the Rideal-Eley mechanism where OH^- reacts from the liquid phase with an adsorbed molecule.
- Ammonia-ammonium equilibrium is reached.

3.1. Combined surface-diffusion controlled process (SDCP) model in the RDE system

A combined surface-diffusion controlled process requires the development of a kinetics expression that accounts for the presence of the adsorbed intermediates as well as a sluggish mass transfer. This mass transfer limitation was added using the experimental effective diffusivity for NH_3 , as the limiting reactant, obtained from the experimental electrochemical tests presented in [23]. The material balance of species i in the axial direction (y) of the RDE system is defined on Eq. 18.

$$-\frac{dN_i}{dy} + R_i - \frac{dC_i}{dt} = 0 \quad (18)$$

where C_i , N_i , and R_i , are the concentration in mol cm⁻³, the flux in mol cm⁻² s⁻¹, and the net generation rate by homogeneous chemical reactions of species i , respectively. The species considered in the model as well as the variables used through the text are presented in Table 1. The flux of species i is affected by three different mass transfer effects which are present in Eq.19: ionic migration, molecular diffusion, and convection [33].

$$N_i = -z(i) \cdot \frac{Ds(i) \cdot F \cdot C_i}{R \cdot T} \cdot \frac{d\phi}{dy} - Ds(i) \cdot \frac{dC_i}{dy} + g_y C_i \quad (19)$$

where ϕ is the potential in the solution (in V vs. Reference Electrode) and T is the temperature. The convection contribution is governed by the flow velocity towards the electrode surface in the axial direction g_y . For the RDE system the axial velocity is defined on Eq. 20 [34].

$$g_y = -0.51\omega^{3/2}\nu^{-1/2}y^2 \quad (20)$$

In order to facilitate the calculations, a dimensionless distance ξ and a dimensionless time τ (Eq. 18-19), were defined in terms of the diffusion layer thickness δ , which was calculated using Eq. 23.

$$\xi = \frac{y}{\delta} \quad (21)$$

$$\tau = \frac{Ds_{NH_3} \cdot t}{\delta^2} \quad (22)$$

$$\delta = 1.61 D_{NH_3}^{1/3} v^{1/6} \omega^{-1/2} \quad (23)$$

Substituting Eqs. 19-23 into equation 18, in the absence of chemical reaction, the mass balance for species $i = K^+, Cl^-,$ and N_2 in the electrolyte media can be described as shown in Eq. 24.

$$\begin{aligned} & \frac{z(i) \cdot F \cdot Ds(i)}{R \cdot T \cdot \delta^2} \left(C_i \frac{d^2 \phi}{d\xi^2} + \frac{dC_i}{d\xi} \cdot \frac{d\phi}{d\xi} \right) + \\ & \frac{Ds(i)}{\delta^2} \frac{d^2 C_i}{d\xi^2} + 0.51 \omega^{3/2} v^{-1/2} \delta \xi^2 \frac{dC_i}{d\xi} - \frac{Ds_{NH_3}}{\delta^2} \frac{dC_i}{d\tau} = 0 \end{aligned} \quad (24)$$

For $i = NH_3, OH^-,$ and NH_4^+ the ammonia dissociation reaction must be included.

Therefore, in order to simplify the calculations, it is assumed that the ammonia dissociation is at equilibrium resulting that $R_{NH_3} = -R_{NH_4^+} = -R_{OH^-}$. Eq. 18 for NH_3 can be added to Eq. 18 for OH^- , and NH_4^+ , respectively, which reduces the mass balances for these three species to two equations consisting of the flux terms as presented in Eqs. 25 and 26. As a consequence of the reduction of the number of equations, the equilibrium expression for the ammonia dissociation needs to be defined (Eq. 27)

$$-\frac{dN_{OH^-}}{dy} - \frac{dC_{OH^-}}{dt} - \frac{dN_{NH_3}}{dy} - \frac{dC_{NH_3}}{dt} = 0 \quad (25)$$

$$-\frac{dN_{NH_4^+}}{dy} - \frac{dC_{NH_4^+}}{dt} - \frac{dN_{NH_3}}{dy} - \frac{dC_{NH_3}}{dt} = 0 \quad (26)$$

$$\frac{C_{NH_4^+} C_{OH^-}}{C_{NH_3}} = K_{eq} \quad (27)$$

In Eqs. 24-27 the unknown variables are the concentration of species i and the potential in the solution versus a reference electrode ϕ . Therefore, the set of governing equations for the $i+1$ variables is completed with the electroneutrality condition Eq. 28.

$$\sum_{i=1}^n z(i) \cdot C_i = 0 \quad (28)$$

To solve the mass balances presented on the previously listed equations, the following boundary conditions are defined:

- At the bulk, $\xi=1$, the boundary conditions are defined by the bulk concentrations for each one of the species and a set value (i.e. $\phi=0.0$ V) for the solution potential. These values were also used as the initial condition to solve the system of equations.
- At the electrode surface $\xi=0$ the flux of species is equal to its rate of consumption or production as expressed in Eq. 29.

$$\frac{s(i) \cdot j}{n \cdot F} + N_i = 0 \quad (29)$$

where $s(i)$ is the stoichiometric coefficient of species i , and j is the current density in A cm^{-2} .

A kinetic expression for the current density of ammonia electrooxidation was developed from the reaction steps described in Eqs. 30 to 34. Eq. 35 was obtained using the r.d.s. approximation in the mechanism described and assuming Eq. 31 (catalytic

dimerization of adsorbed NH_2) as the r.d.s. The procedure followed for the derivation of equation 35 is explained in detail in the supporting information file.

$$j = \left(\frac{EASA}{EGA} \right) n \cdot F \cdot k_{2f} K_1^2 C_{\text{NH}_3}^2 C_{\text{OH}^-}^2 \cdot e^{\frac{2F(Vd - f - Ujref_1)}{RT}} \cdot \left(1 + K_1 C_{\text{NH}_3} C_{\text{OH}^-} e^{\frac{F(Vd - f - Ujref_1)}{RT}} + K_1 K_4 C_{\text{NH}_3} C_{\text{OH}^-}^2 e^{\frac{F(2Vd - 2f - Ujref_1 - Ujref_4)}{RT}} + K_5 K_4 K_1 C_{\text{NH}_3} C_{\text{OH}^-}^3 e^{\frac{F(3Vd - 3f - Ujref_1 - Ujref_4 - Ujref_5)}{RT}} \right)^2 \quad (35)$$

The $Ujref_i$ variables on Eq. 35 (and also in Eq. 41) represent the formal potential for each electrochemical reaction respectively, which can be calculated as shown in reference [35]. However, in this work the formal potentials are treated as adjustable parameters since apart from the electrooxidation of hydrazine the standard reduction potentials for the other electrochemical reactions are unknown.

3.2. Surface confined process (SCP) model in the RDE system

For the development of a surface confined reaction model, the adsorbed intermediates should be added as implicit variables within the model. The addition of new variables, associated to species present exclusively on the surface of the electrodes, requires the modification of the boundary conditions mostly at $\xi=0$ along with the addition of the same number of equations and variables in the central nodes and outer boundary $\xi=1$. The required equations on the electrode surface come from the individual balances of each species obtained from Eqs. 30 to 34. In order to reduce the number of parameters to the minimum possible Eq. 31 was still considered as the r.d.s. for the formation of N_2 , whereas Eqs. 30, 33, and 34 were not longer considered to be in equilibrium. The individual mass balances for the adsorbed intermediates are presented in Eq. 36 to 38, where Γ is the maximum surface concentration of active sites in mol cm^{-2} calculated from the adsorption charge associated to a monolayer of hydrogen ($210 \mu\text{C cm}^{-2}$) [36], and $\theta_{(NH_2, NH, N)}$ are the fractional coverage of the adsorbed intermediates. Eq. 39 accounts for the balance of active sites where θ is the fraction of available active sites.

$$\begin{aligned}
& k_{1f} C_{NH_3} C_{OH^-} q \times e^{\frac{\alpha_1 \cdot F \cdot \eta_1}{R \cdot T}} - k_{1b} q_{NH_2} \times e^{-\frac{(1-\alpha_1) \cdot F \cdot \eta_1}{R \cdot T}} - k_{4f} q_{NH_2} \times C_{OH^-} \times e^{\frac{\alpha_4 \cdot F \cdot \eta_4}{R \cdot T}} \\
& + k_{4b} q_{NH} \times e^{-\frac{(1-\alpha_4) \cdot F \cdot \eta_4}{R \cdot T}} - k_{2f} q_{NH_2}^2 = \frac{G \cdot dq_{NH_2}}{dt}
\end{aligned} \tag{36}$$

$$\begin{aligned}
& k_{4f} \theta_{NH_2} C_{OH^-} \cdot e^{\frac{\alpha_4 \cdot F \cdot \eta_4}{R \cdot T}} - k_{4b} \theta_{NH} \cdot e^{-\frac{(1-\alpha_4) \cdot F \cdot \eta_4}{R \cdot T}} - k_{5f} \theta_{NH} C_{OH^-} \cdot e^{\frac{\alpha_5 \cdot F \cdot \eta_5}{R \cdot T}} \\
& + k_{5b} \theta_N \cdot e^{-\frac{(1-\alpha_5) \cdot F \cdot \eta_5}{R \cdot T}} = \frac{\Gamma \cdot d\theta_{NH}}{dt}
\end{aligned} \tag{37}$$

$$k_{5f} \theta_{NH} C_{OH^-} \cdot e^{\frac{\alpha_5 \cdot F \cdot \eta_5}{R \cdot T}} - k_{5b} \theta_N \cdot e^{-\frac{(1-\alpha_5) \cdot F \cdot \eta_5}{R \cdot T}} = \frac{\Gamma \cdot d\theta_N}{dt} \tag{38}$$

$$1 = \theta + \theta_{NH_2} + \theta_{NH} + \theta_N \tag{39}$$

It can be observed in Eq. 36 to 38 that reactions 1, 4, and 5 are not longer considered in equilibrium with reaction 2, the r.d.s. for the formation of N₂. On the other hand, the equilibrium condition was still maintained for reaction 3 regarding reaction 2 so that the N₂ production rate can still be considered as that of reaction 2. Therefore, more than one current term needs to be included in the quantification of the current density. A more general expression for the boundary condition in Eq. 29 is presented in Eq. 40. This expression can therefore be applied when there is more than one electrochemical reaction taking place at the same time.

$$\sum_{r=1}^{reac} s(i, r) \cdot \frac{j_r}{n_r \cdot F} + N_i = 0 \quad (40)$$

where n_r is the number of electrons transferred, $s(i, r)$ is the stoichiometric coefficient of the dissolved species, and j_r is the current density of reaction r , respectively.

The current density expression developed for the surface confined process is presented in Eq. 41. Notice that each one of the terms inside the outer parenthesis on Eq. 41 represents the contribution to the current density from each one of the reactions (Eqs. 36-

$$38) \quad j = \left(\frac{EASA}{EGA} \right) F \left(\begin{array}{l} n_1 \left(k_{1f} C_{NH_3} C_{OH^-} \theta \cdot e^{\frac{\alpha_1 \cdot F \cdot (Vd - \phi - Ujref_1)}{R \cdot T}} - k_{1b} \theta_{NH_2} \cdot e^{\frac{(1-\alpha_1) \cdot F \cdot (Vd - \phi - Ujref_1)}{R \cdot T}} \right) \\ + n_2 k_{2f} \theta_{NH_2}^2 + n_4 \left(k_{4f} \theta_{NH_2} C_{OH^-} e^{\frac{\alpha_4 \cdot F \cdot (Vd - \phi - Ujref_4)}{R \cdot T}} - k_{4b} \theta_{NH} \cdot e^{\frac{(1-\alpha_4) \cdot F \cdot (Vd - \phi - Ujref_4)}{R \cdot T}} \right) \\ + n_5 \left(k_{5f} \theta_{NH} C_{OH^-} \cdot e^{\frac{\alpha_5 \cdot F \cdot (Vd - \phi - Ujref_5)}{R \cdot T}} - k_{5b} \theta_N \cdot e^{\frac{(1-\alpha_5) \cdot F \cdot (Vd - \phi - Ujref_5)}{R \cdot T}} \right) \end{array} \right) \quad (41)$$

The governing equation for the central nodes and outer boundary can be expressed as in Eq. 42

$$\frac{d\theta_{(NH_2, NH, N)}}{dy} = 0 \quad (42)$$

3.3. Solution methodology

The current density expressions on Eqs. 35 and 41 were substituted into Eq. 29 for each one of the cases under analysis. The systems of nonlinear differential equations were discretized applying finite differences for the space dimension and the implicit method for the time dimension. The discretized equations and their jacobians were generated using Maple 14 by extending subroutines developed by Botte [37, 38]. Then, the systems of nonlinear equations were linearized using the Band-J subroutine [33, 39] and solved using the lower upper decomposition method (LUDEC). Both the Band-J and LUDEC subroutines were implemented in Fortran.

The unknown parameters for each one of the cases under study were adjusted, using the Gauss-Marquardt-Levenberg method in the software Winpest 3.0.0 [38], against the experimental data obtained from the RDE and LSV experiments in a 0.1 M KOH + 0.01 M NH₄Cl solution performed as presented elsewhere [23]. PEST optimizes the value of the parameters by comparing simulated data with experimental data. A total of 302 experimental values obtained by LSV were used for the estimation of the parameters. The software minimizes the differences between the data using a least squares minimization procedure based on the Levenberg–Marquardt algorithm. The values of the fixed parameters and transport properties used for both models are presented in the Table 1 while

the values of the adjusted parameters, which minimized the sum of the square root of the residuals providing the best possible fit of the experimental data, are shown in Table 2. The two models developed in this paper were discriminated using the Wilks and Williams test coupled with the t-test [40].

4. Results

The results for the best parameter fittings obtained from the kinetics models in Eq. 35 and 41 are shown in Fig. 2. Correlation coefficients of $R^2=0.992$ and $R^2=0.999$ were obtained for the combined surface-diffusion controlled model and the surface confined model respectively, with the parameters presented on Table 2. A sensitive analysis, not presented here, allowed to establish that the cathodic current contributions due to reactions 1, 4, and 5 are not affecting the modeling results, therefore no changes in the predicted current density were observed when the parameters k_{1b} , k_{4b} , and k_{5b} were removed from the model.

Although low sensitivity was also observed from the anodic contribution of reactions 4 and 5, their reaction parameters were still considered while it was not possible to obtain a good model fitting when they were removed from Eq. 41. The low dependence of the final model to the removed parameters can be explained from the low reaction rates and the over potentials in which the reactions are taking place rather than the irreversible nature of the ammonia electrooxidation process. These parameters could still be important if a CV model were developed since a cathodic peak attributed to the reduction of adsorbed intermediates back to NH_3 (peak C2 on shown in Fig. 1) can be observed [11].

The Wilks and Williams test, along with the t-test [40], were used to evaluate the significance of the models and discriminate among the two different regression equations as presented in [38]. The results of the b constants presented in Table 2 show a higher value for the surface confined model than the combined surface-diffusion controlled model. A higher b value stands for a higher effectiveness for the surface confined model to fit the experimental data. Moreover, the one tailed t value higher than t at $\alpha_t = 0.05$ rejects the null hypothesis that both models have the same prediction level of the independent value (current density). Therefore, the surface confined prediction model is a better representation of the phenomena taking place during the ammonia electrooxidation, which discards that mass transfer effects could play any role in the reaction kinetics in the RDE.

Once the parameters were fitted, the ability of the models to predict the current profiles at different scan rates was tested. While the SDCP model was unable to predict changes in current profiles at different scan rates, the SCP model can predict increases in the current peak and peak potential as featured in the experimental results reported elsewhere [23]. However, a satisfactory fit of the experimental values at different scan rates was only obtained when the values for the reaction constants of the first electron transfer reaction (k_{1f} in reaction 1) and the reaction constant of the r.d.s. towards the production of N_2 (k_{2f} in reaction 2) as presented in Fig. 3 were changed. Dependence of the calculated reaction constants obtained from potential sweep experiments at different scan rates have been reported in other papers [41, 42]. The differences in the calculated reaction constants at different scan rates could be explained from the theory developed by Nicholson and Shain [43], which describes the dependence of both a dimensionless rate

parameter (ψ) and the shape of the current profiles, with the potential scan rate. In the particular case of a catalytic reaction following an irreversible electron transfer reaction, as it is the case for the mechanism proposed in this work for ammonia electrooxidation, the reaction constants can be calculated applying the Nicholson method from Eq. 43 [43, 44], where n_α are the total number of electrons transferred before the r.d.s.

$$k = \psi(v) \frac{\alpha n_\alpha F v}{RT} \quad (43)$$

As shown in Eq. 43 the scan rate independent rate constant can be obtained from the potential sweep experiments if ψ is known. Nicholson and Shain [43, 44] have tabulated several ψ values for different scan rates. However, no values for $0.04 < \psi$ are reported, and the ψ values expected from the small rate constant values fitted from the model are lower than that. Therefore, $\psi(v)$ was calculated from the observed rate constants k_{1f} and k_2 using Eq. 43. The scan rate independent rate constants for reaction 1 ($k_{1f}^0 = 1.23 \times 10^{-4} \text{ cm}^4 \text{ s}^{-1} \text{ mol}^{-1}$) and reaction 2 ($k_{2f}^0 = 3.66 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$) were obtained from the slopes in Figs. 4 a and b, respectively.

The surface confined model also provides a quantitative and qualitative description of the coverage distribution of adsorbed intermediates at different potentials, along with the contribution of the different reactions to the final current profile observed during the LSV experiments. Fig. 5 and Fig. 6 present the current-potential profiles for the different reactions considered within the mechanism developed in this paper (Eq. 30 to 34) at

different scan rates, and the adsorbed intermediates' fractional coverage dependence with the potential at different scan rates, respectively.

The results indicate that the main reason for the decrease in the current density in the ammonia electrooxidation current potential profiles is the successive dehydrogenation of ammonia to form adsorbed imine -NH and atomic nitrogen therefore decreasing the number of active sites in the catalyst at applied potentials higher than -0.2 V vs. Hg/HgO in a 0.1 M KOH + 0.01 M NH₄Cl. The results obtained with the model agree with the experimental and phenomenological description of the ammonia electrooxidation process provided by different authors in previous works [12, 13, 15, 19, 28], and contributes to corroborate that the electrooxidation of ammonia in Pt towards nitrogen is an slow surface kinetics control process, which takes place through the catalytic dimerization of partially dehydrogenated NH₃ adsorbed intermediates to hydrazine like adsorbates (Eq. 31). Therefore, the electrooxidation of ammonia to nitrogen proceeds in an electrochemical followed by catalytic (EC') reaction mechanism (additional experimental evidence is presented in the supporting information file), where the catalytic process was identified as the r.d.s.

5. Conclusions

A mathematical model for the ammonia electrooxidation in a Pt RDE system was developed based on the micro kinetics approach. The ammonia electrooxidation reaction was observed to be a surface confined kinetics process where the decrease of current density reported in the literature even at high rotation rates can be attributed to the effect of

adsorbed intermediates and the deactivation of the Pt catalyst by the successive dehydrogenation of NH_3 adsorbates.

The electrooxidation of ammonia mechanism towards nitrogen was found successfully modeled to follow an electrochemical followed by a catalytic (EC') reaction mechanism where the catalytic process which was considered to be the catalytic dimerization of adsorbed amine $-\text{NH}_2$ to form hydrazine was identified as the r.d.s. In general slow reaction rates were identified over polycrystalline Pt catalyst. A kinetics expression along with kinetics parameters such as reaction rates constants for the different steps relevant to the micro kinetics steps considered in this paper were obtained, which can be later use for the process simulation, electrolyzer design and scale up.

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Table 1. Fixed model parameters.

Table 2. Estimated model kinetics parameters.

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Fig. 1 Open window cyclic voltammetry for ammonia electrooxidation in 0.1 M KOH + 0.01 M NH₄Cl at 50 mV s⁻¹ (continuous lines) and 0.1 M KOH (dashed line). The peaks A1 and C1 are attributed to reversible NH₃ adsorption. Peak A₂ is recognized to ammonia electrooxidation. Peak C2 is observed when the applied potential overcomes the ammonia electrooxidation onset potential, therefore recognized as the reduction of surface intermediates. Another peak C3 is observed when high upper limit potentials are reached and is attributed to the reduction of NO-kind components [15].

Fig. 2 Comparison of the LSV curves obtained by the combined SDGP model (solid thin line), the SCP model (solid thick line), and the experimental results (dotted line) at 10 mV s⁻¹ and 1000 rpm in a 0.1 M KOH + 0.01 M NH₄Cl solution. A better representation of the experimental data was obtained with the surface confined model.

Fig. 3 Results obtained for the SCP model of ammonia electrooxidation LSV at different scan rates and 1000 rpm. Experimental values (dotted lines), Predicted values (continuous lines). Parameter values are as reported in Table 2 except for $k_{1f}=1.46 \times 10^{-4} \text{ cm}^4 \text{ s}^{-1} \text{ mol}^{-1}$ and $k_{2f}=4.16 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$ at $\nu=0.01 \text{ V s}^{-1}$, $k_{1f}=1.97 \times 10^{-4} \text{ cm}^4 \text{ s}^{-1} \text{ mol}^{-1}$ and $k_{2f}=5.34 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$ at $\nu=0.03 \text{ V s}^{-1}$, and $k_{1f}=2.30 \times 10^{-4} \text{ cm}^4 \text{ s}^{-1} \text{ mol}^{-1}$ and k_{2f}

$=6.00 \times 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$ at $\nu = 0.05 \text{ V s}^{-1}$. The SCP model can predict the dependence of the LSV profile with the scan rate validating the application of the model.

Fig. 4 Dimensionless rate parameters $\psi(\nu)$ obtained from the fitted kinetics parameters a) k_{1f} and b) k_{2f} at different scan rates. $b = \alpha n_{\alpha} F \nu / RT$. The linear dependence of the dimensionless rate parameter with the scan rate was used to calculate the scan rate independent rate constants k_{1f}^0 and k_{2f}^0 .

Fig. 5 Current potential profiles for the different reactions taking place in the ammonia electrooxidation mechanism at different scan rates. a) reaction 1, b) reaction 2-3, c) reaction 4, and d) reaction 5. The highest contribution toward the total current density in the potential range from -0.2 to -0.1 V vs. Hg/HgO is due to the formation of N_2 . However, the current contribution due to the successive dehydrogenation of adsorbed intermediates increases along with the applied potential.

Fig. 6 Fractional coverage of the predicted adsorbed intermediates at different scan rates. a) θ_{NH_2} , b) θ_{NH} , c) θ_{N} , and d) free space θ . NH_2 is the predominant adsorbed intermediate within the potential region studied.

Table 1.

SYMBOL	PARAMETER NAME	VALUE
nj	Number of nodes in the y dimension	100
T	Temperature (K)	298.15
R	Universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)	8.314
F	Faraday's constant (C mol^{-1})	96482
ω	Disk rotation speed (rpm)	1000
Cutoff	Cutoff potential (V)	-0.10
iniV	Initial potential (V)	-0.40
nt	number of data points in the output (dimensionless)	604
EASA	Electrode active surface area (cm^2)	2.33 [23]
EGA	Electrode geometric area (cm^2)	1.96×10^{-1} [23]
ν^+	kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$)	7.79×10^{-3}
Ds(1)^{+,++}	diffusion coefficient of NH_3 ($\text{cm}^2 \text{s}^{-1}$)	2.65×10^{-5} , 2.65×10^{-6}
Ds(2)⁺	diffusion coefficient of OH^- ($\text{cm}^2 \text{s}^{-1}$)	5.22×10^{-5}
Ds(3)⁺	diffusion coefficient of K^+ ($\text{cm}^2 \text{s}^{-1}$)	1.94×10^{-5}
Ds(4)⁺	diffusion coefficient of Cl^- ($\text{cm}^2 \text{s}^{-1}$)	2.01×10^{-5}
Ds(5)⁺	diffusion coefficient of N_2 ($\text{cm}^2 \text{s}^{-1}$)	3.62×10^{-5}
Ds(6)⁺	diffusion coefficient of NH_4^+ ($\text{cm}^2 \text{s}^{-1}$)	1.94×10^{-5}
z(i)	charge number of component i (dimensionless)	0,-1,1,-1,0, and 1
cb(1)	bulk concentration of NH_4Cl (mol cm^{-3})	1.00×10^{-5}
cb(2)	bulk concentration of KOH (mol cm^{-3})	1.00×10^{-4}
n	Total electrons transferred in ammonia electrolysis	9
n₁	number of electrons transferred reaction 1 (dimensionless)	1
n₂	number of electrons transferred reaction 2 and 3 (dimensionless)	4
n₄	number of electrons transferred reaction 4 (dimensionless)	1
n₅	number of electrons transferred reaction 5(dimensionless)	1
ν	scan rate (V s^{-1})	0.01, 0.03, and 0.05
K_{eq}	NH_3 dissociation constant (mol cm^{-3})	1.99×10^{-8}
Γ	Surface concentration (mol cm^{-2})	2.18×10^{-9}
α_1	Transfer coefficient reaction 1	0.5
α_4	Transfer coefficient reaction 4	0.5
α_5	Transfer coefficient reaction 5	0.5

⁺Transport properties such as kinematic viscosity and diffusion coefficient were calculated in Aspen Properties using the Electrolyte-NRTL activity coefficient method with the SRK equation of state.

⁺⁺The second value reported for NH_3 diffusion coefficient was the value used for the SDCP approximation and was obtained from the experimental data presented in Ref. [23] as shown in the

supporting documentation.

Table 2.

	SDCP	SCP	Units
<i>Ujref</i>	-0.74	-0.68	V
<i>Ujref₄</i>	-0.24	-0.21	V
<i>Ujref₅</i>	-0.20	-0.34	V
<i>k_{1f}</i>	-	1.46x10 ⁻⁴	cm ⁴ s ⁻¹ mol ⁻¹
<i>K₁</i>	10	-	cm ⁶ mol ⁻²
<i>k_{2f}</i>	1.80x10 ⁻¹⁰	4.16x10 ⁻¹⁰	mol cm ⁻² s ⁻¹
<i>k_{4f}</i>	-	2.87x10 ⁻⁷	cm s ⁻¹
<i>K₄</i>	8.91	-	cm ³ mol ⁻¹
<i>k_{5f}</i>	-	2.08x10 ⁻⁷	cm s ⁻¹
<i>K₅</i>	2.24x10 ⁻²	-	cm ³ mol ⁻¹
b	0.1105	0.8895	-
D.F.⁺	301	301	-
t calculated		54.53	
t at $\alpha_t=0.05$		1.65	

⁺ Degrees of freedom (n-p+1). n= number of data, p number of equations

Fig. 1. Diaz and Botte.

Fig. 2. Diaz and Botte.

Fig. 3. Diaz and Botte

Fig. 4. Diaz and Botte.

Fig. 5. Diaz and Botte.

Fig. 6. Diaz and Botte.

Diaz and Botte