Mathematical model of a parallel plate ammonia electrolyzer for combined wastewater remediation and hydrogen production

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ABSTRACT

A mathematical model was developed for the simulation of a parallel plate ammonia electrolyzer to convert ammonia in wastewater to nitrogen and hydrogen under basic conditions. The model consists of fundamental transport equations, the ammonia oxidation kinetics at the anode, and the hydrogen evolution kinetics at the cathode of the electrochemical reactor. The model shows both qualitative and quantitative agreement with experimental measurements at ammonia concentrations found within wastewater (200–1200 mg L^{-1}).
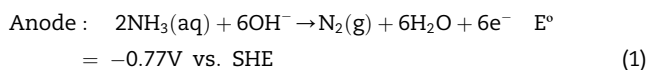
The optimum electrolyzer performance is dependent on both the applied voltage and the inlet concentrations. Maximum conversion of ammonia to nitrogen at the rates of 0.569 and 0.766 mg L^{-1} min^{-1} are achieved at low (0.01 M NH$_4$Cl and 0.1 M KOH) and high (0.07 M NH$_4$Cl and 0.15 M KOH) inlet concentrations, respectively. At high and low concentrations, an initial increase in the cell voltage will cause an increase in the system response – current density generated and ammonia converted. These system responses will approach a peak value before they start to decrease due to surface blockage and/or depletion of solvated species at the electrode surface. Furthermore, the model predicts that by increasing the reactant and electrolyte concentrations at a certain voltage, the peak current density will plateau, showing an asymptotic response.

1. Introduction

Ammonia electrolysis is undergoing development as a viable technology for wastewater remediation (Boggs and Botte, 2009; Botte, 2010; Kim et al., 2006; Reyter et al., 2010). NH$_3$ and other nitrogen compounds in water can cause eutrophication which endangers aquatic life (Feng et al., 2003). On the other hand, ammonia is a good source of hydrogen for energy generation (Boggs and Botte, 2010; Botte, 2012a, b, c; Cooper and Botte, 2006; Muthuvel and Botte, 2009; Vitse et al., 2005). Using an electrolytic cell, ammonia is oxidized at the anode and water is reduced at the cathode for an overall reaction that produces benign nitrogen and useful hydrogen according to Equations (1)–(3) (Diaz and Botte, 2012):
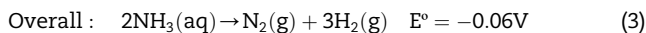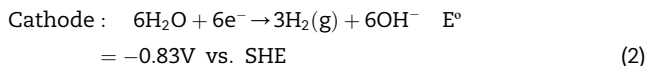
$$\text{Anode}: \quad 2\text{NH}_3(\text{aq}) + 6\text{OH}^- \rightarrow \text{N}_2(\text{g}) + 6\text{H}_2\text{O} + 6\text{e}^- \quad \text{E}^\circ$$
$$= -0.77\text{V} \text{ vs. SHE} \tag{1}$$

Cathode : $6H_2O + 6e^- \rightarrow 3H_2(g) + 6OH^-$ E°
$$= -0.83V \text{ vs. SHE} \tag{2}$$

Overall : $2NH_3(aq) \rightarrow N_2(g) + 3H_2(g)$ E° = -0.06V   (3)

The potentials of the electrode reactions (1) and (2) are shown as reduction potentials vs. standard hydrogen electrode (SHE). In comparison, water electrolysis for hydrogen production would require an overall voltage of −1.23 V; therefore ammonia electrolysis would provide a theoretical saving of 95% in energy consumption. The oxidation of ammonia to nitrogen takes place at a cell voltage much lower than water (0.06 V instead of 1.23 V), and therefore ammonia in water can be selectively oxidized and removed to generate non-toxic nitrogen and hydrogen (Botte, 2010; Botte et al., 2009).

Literature on ammonia electrolysis has encompassed proposed mechanisms (Gerischer and Mauerer, 1970; Oswin and Salomon, 1963), electrode morphology (Vidal-Iglesias et al., 2003; 2005), and theoretical calculations (Skachkov et al., 2013). Recent studies using both electronic structure calculations (Daramola and Botte, 2012, 2013) and electrochemical techniques (Diaz et al., 2013; Palaniappan and Botte, 2013) have provided insight into relevant phenomena including, surface sensitivity of this reaction which was confirmed by Rosca and Koper (2006), surface adsorption of different intermediates such as NH_2, N_2H_4, NH, N_2H_2, … and N (Daramola and Botte, 2013; Rosca and Koper, 2008), and deactivation of the platinum anode as well as reaction kinetics at both electrodes due to the presence of ammonia (Daramola and Botte, 2012; de Vooys et al., 2001; Palaniappan and Botte, 2013).

At the cathode, it has been shown that the hydrogen evolution reaction (HER) could proceed in three steps (Lasia, 1989):

- Electroreduction of water to adsorbed hydrogen atom and hydroxide ion; also known as the Volmer reaction, Equation (4):

$$M + H_2O + e^- \underset{k_{1b,c}}{\overset{k_{1f,c}}{\rightleftarrows}} MH + OH^- \tag{4}$$

- Electroreduction of water on adsorbed sites of hydrogen to produce hydrogen gas and hydroxide ions, also known as the Heyrovsky reaction, Equation (5):

$$MH + H_2O + e^- \underset{k_{2b,c}}{\overset{k_{2f,c}}{\rightleftarrows}} M + H_2 + OH^- \tag{5}$$
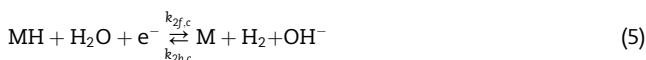
- Chemical desorption of hydrogen; also known as the Tafel reaction, Equation (6):

$$2MH \underset{k_{3b,c}}{\overset{k_{3f,c}}{\rightleftarrows}} 2M + H_2 \tag{6}$$

Using experiments performed on nickel in 1 M NaOH, Lasia and Rami showed that the HER proceeds via reactions (4) and (5), (Volmer–Heyrovsky mechanism) (Lasia and Rami, 1990). In addition, Hitz and Lasia used the galvanostatic pulse

method to determine the rate constant of the HER based on the Volmer–Heyrovsky mechanism (Hitz and Lasia, 2002). On the other hand, Kreysa et al. used iR-corrected steady-state polarization curves to show that the HER follows the Volmer–Tafel mechanism, and reported rate constants for the forward and backward reactions (Kreysa et al., 1988). Moreover, using a combination of classical steady state voltammetry and impedance spectroscopy, Krstajic et al. showed that within the potential region −1.1 < E < −0.95 vs. SHE, the HER mechanism is initially the Volmer reaction followed by the Tafel reaction, with negligible contribution from the Heyrovsky reaction (Krstajic et al., 2001). At potentials E < −1.2 V, a Tafel line with a slope of approximately −0.121 V dec^{-1} was obtained. This finding suggested that, in this potential region, the HER mechanism is a consecutive combination of the Volmer and Heyrovsky reactions, with negligible contribution of the Tafel reaction. In summary, it can be concluded that the HER mechanism is highly dependent on the applied potential.

At the anode, the ammonia oxidation mechanism has also been highly debated by researchers. Oswin and Salomon proposed that ammonia is converted to dinitrogen, through stepwise dehydrogenation and recombination of nitrogen atoms (Oswin and Salomon, 1963). Subsequently, Gerischer and Mauerer observed that at potentials higher than 0.6 V vs. RHE (reversible hydrogen electrode) the platinum electrode became deactivated. An *ex situ* analysis of a deactivated electrode, using temperature programmed desorption, indicated that adsorbed nitrogen atoms was the source of deactivation (Gerischer and Mauerer, 1970). de Vooys et al. also demonstrated that formation of atomic nitrogen is the reason for catalytic deactivation (de Vooys et al., 2001). In a later study, Rosca and Koper studied the mechanism of reaction by using voltammetry, chronoamperometry and *in situ* infrared spectroscopy (Rosca and Koper, 2006). The authors claimed that the mechanism of ammonia oxidation can occur through formation of surface hydrazine and that N_2H_4 adsorbed may play a promising role in dinitrogen formation. Using these results, a mathematical model of ammonia electrooxidation kinetics in a rotating disk electrode system was developed by Diaz and Botte (in press).

In summary, both ammonia oxidation and hydrogen evolution reactions have been examined with a variety of techniques at the atomic or bench scale. However, a macroscale model that combines thermodynamics, kinetics, and flow profiles would be more useful for predicting electrolyzer properties for scale-up including conversion of reactants, selectivity of reactions, and current developed-to determine power and energy consumption (White et al., 1983). This would be essential when considering large scale application of this technology where momentum, mass and heat transfer effects will be relevant and factors such as catalyst and reactor configuration affect the performance of the reactor (Santhanagopalan and White, 2010).

Within this context, this paper seeks to examine wastewater remediation by ammonia electrolysis using a mathematical model based on a parallel-plate electrochemical reactor configuration. This mathematical model combines electrode kinetics, fundamental transport equations of reactor species and bench-scale experiments to yield a semi-