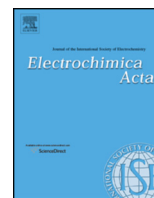




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Hydrodynamic analysis and simulation of a flow cell ammonia electrolyzer

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ABSTRACT

The hydrodynamic analysis and simulation of a non-ideal single pass flow cell alkaline ammonia electrolyzer was performed after the scale-up of a well-characterized deposited polycrystalline Pt on Ni anode. The hydrodynamic analysis was performed using the residence time distribution (RTD) test. The results of the hydrodynamic investigation provide additional insights for the kinetic analysis of the ammonia electrooxidation reaction on polycrystalline Pt electrocatalysts -which are typically obtained under controlled flow regime, e.g., rotating disk electrode- by including the flow non-uniformity present in the electrolyzer. Based on the RTD function, the ammonia electrolyzer performance was simulated as a non-steady stirred tank reactor (CSTR) and the unknown kinetic parameters were obtained by fitting the simulation results with an experimental current profile, obtaining an adequate prediction of the ammonia conversion. This simplified approach for the simulation of the ammonia electrolyzer could be implemented in process simulation packages and could be used for the design and scale-up of the process for hydrogen production and wastewater remediation.

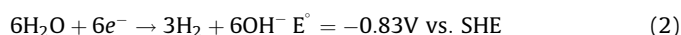
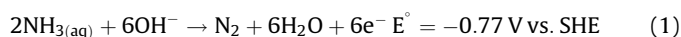
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1. Introduction

The oxidation of ammonia by means of electrochemical methods on Pt electrodes is an important reaction due to its application in different processes, such as the development of ammonia sensors [1], energy production through direct ammonia fuel cells [2], the removal of ammonia from domestic wastewater, and the treatment of industrial ammonia emissions [3]. Moreover, liquid ammonia is a promising alternative for hydrogen production [4,5] due to its high volumetric hydrogen density (45% higher volumetric hydrogen density than liquid hydrogen [6]) and high specific energy density in kWh L⁻¹ (50% higher energy density than liquid hydrogen [7–9]).

When ammonia electrooxidation in alkaline media (Eq. (1)) is coupled with water reduction (Eq. (2)), in a process known as ammonia electrolysis (Eq. (3)) [10], it is theoretically possible to produce hydrogen with just five percent of the energy required from water electrolysis [8,9]. However, the lack of understanding of the reaction mechanism and kinetics has not allowed the full

utilization and implementation of the technology in processes such as the electrochemical deammonification of wastewater [3].



Diaz and Botte examined the intrinsic kinetics associated with the ammonia electrooxidation reaction in deposited polycrystalline Pt [11]. The authors developed a kinetic model, based on the reaction mechanism proposed by Gerischer and Mauerer [12], which accounts for two parallel reaction pathways. After the first dehydrogenation of ammonia, to absorbed amine (-NH₂), the formation of molecular nitrogen proceeds through the dimerization of amine to form hydrazine, which is subsequently oxidized to molecular nitrogen (N₂). At the potentials where ammonia electrooxidation takes place the oxidation of hydrazine is a fast process and can be considered as the irreversible step for the formation of molecular nitrogen [13]. On the other hand, the parallel reaction pathway follows the consecutive

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dehydrogenation of amine to atomic nitrogen, which ends with the deactivation of the active sites in the electrode. The model considers that ammonia is the only reactant adsorbed on the active sites, following an Eley-Rideal mechanism; therefore, the hydroxyl ions (Eq. (1)) are not adsorbed and react from the solution.

The ammonia electrooxidation model developed by Diaz and Botte [11] was verified with the mathematical simulation of linear sweep voltammetry (LSV) experimental data in a well-defined hydrodynamic system, such as the rotating disk electrode (RDE). The authors obtained heterogeneous reaction kinetic constants through multiple parameters estimation with correlation coefficients of at least $R^2=0.999$ against experimental data. It was concluded that the ammonia electrooxidation kinetics in polycrystalline Pt is a surface controlled process. Peak currents below the diffusion limiting current and the decay of the anodic current obtained during voltammetry experiments on polycrystalline Pt [14] (even at high rotational rates), are caused by the formation of deactivating adsorbates, such as adsorbed imine (NH-) and atomic nitrogen (N). By means of the elucidation of the intrinsic kinetics obtained in the RDE electrodes it was expected to contribute to the design and scale up of the electrolyzer and deposited polycrystalline Pt electrode.

However, in real world applications well define hydrodynamic conditions (as those obtained in the RDE system) are never obtained, therefore the simulation of the performance of the electrochemical reactor has to account for non-uniformity of the fluid flow, dead volumes, and inlet effects that affect the mass transfer of the species. Consequently, the identification of a well-

known reactor model –such as plug flow reactor (PFR), continuous stirred tank reactor (CSTR), laminar reactor, etc.– is required for the establishment of mass balances [15]. In this paper, the hydrodynamic analysis of an ammonia single flow cell electrolyzer was performed in order to provide further insights of the ammonia electrooxidation reaction in a non-ideal reactor. The analysis extends an ammonia electrooxidation kinetic model, developed in previous research [11], to account for non-ideal flow conditions. The experimental approach included the scale-up of a well characterized Pt deposited on Ni substrate anode [11,14], the analysis of the effect of the cathode in the ammonia electrooxidation using either Pt or Ni as cathodes, and the determination of the residence time distribution (RTD) function of the electrochemical reactor (which allows a characterization of the mixing behavior occurring within the electrolyzer and its effect on the ammonia electrolysis). The results obtained from the RTD analysis led to the simulation of the electrolyzer as a simple non-steady continuous stirred tank reactor (CSTR). The simulation results of the predicted conversion profile validated the use of the CSTR model to describe the performance of the ammonia electrolyzer for the tested hydrodynamic conditions.

2. Experimental

2.1. Electrode preparation

A 14.8 cm × 14.8 cm Ni gauze, Alfa Aesar 40 mesh woven, framed in a 0.25 cm thick border of Ni foil (Alfa Aesar 0.0127 cm

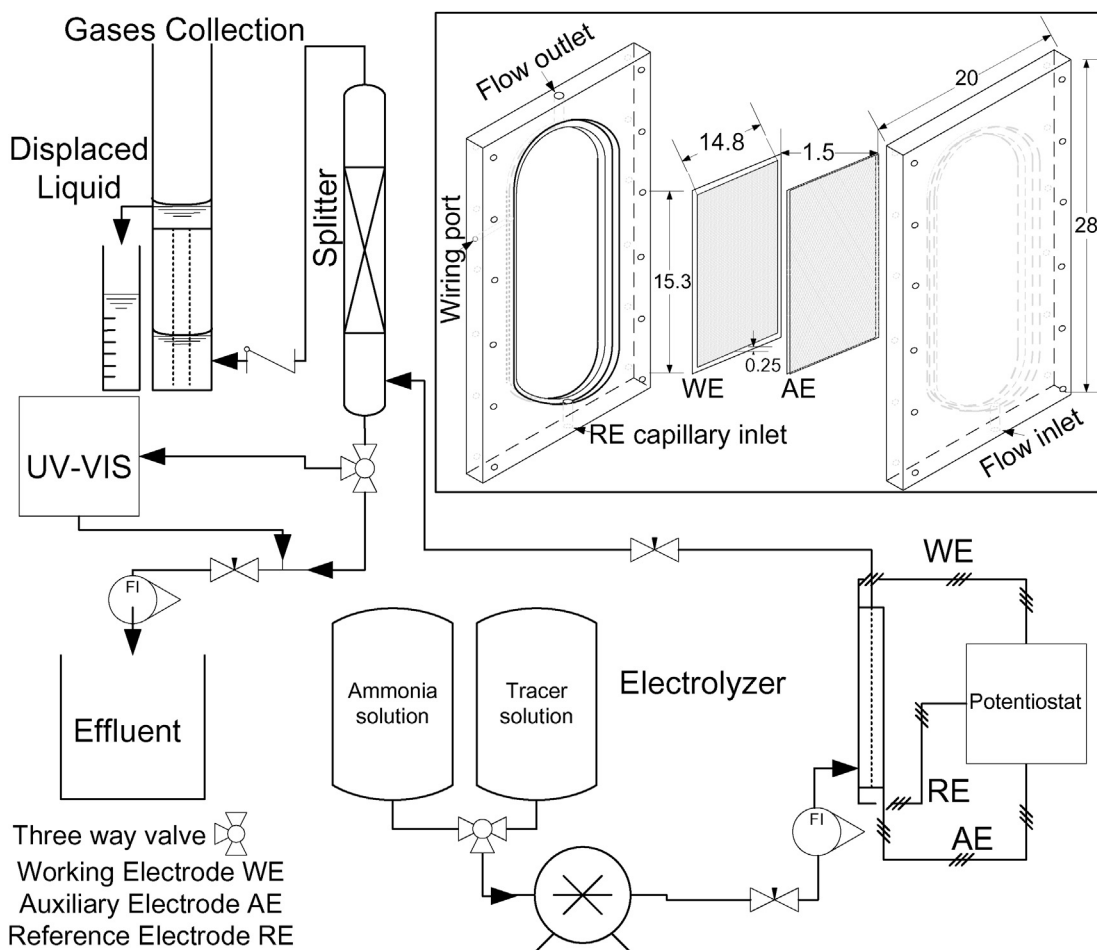


Fig. 1. Ammonia electrolysis set up used for the RTD experiments. A constant level of fluid was kept in the upper chamber of the gas collection system to maintain the pressure constant inside the electrolysis system. Insert parallel plate electrolyzer parts and configuration. Dimension units are in cm.

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