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AMBIENT TEMPERATURE GAS PHASE ELECTROCHEMICAL NITROGEN REDUCTION TO AMMONIA AT RUTHENIUM / SOLID POLYMER ELECTROLYTE INTERFACE

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The direct gas phase electrochemical reduction of nitrogen to ammonia is reported at ruthenium/solid polymer electrolyte interface using cells of the general configuration

N_2, Ru/Nafion 417/Pt, Ar(90%), H_2(10%).

The Faradaic efficiency for reducing nitrogen to ammonia was found to be 0.0015% at a current density of 3.12 mA/cm^2 corresponding to 1.75×10^{-9} moles cm^{-2}h^{-1} on a 9.65 cm^2 electrode. Substitution of N_2 by Ar in the cathode chamber of these cells gave no detectable ammonia, suggesting introduced N_2 as the source used during NH_3 synthesis.

1. Introduction

Recent work reported by ourselves and others [1] has shown that CO_2 can be electrochemically reduced in the gas phase to give predominantly the gaseous hydrocarbons ethylene and ethane, using cells of the general configuration

CO_2, Cu/Nafion/Pt, H_2.

We have observed Faradaic efficiencies up to 21% at current densities of 30 mA/cm^2. Subsequent work [2–4] has suggested that CO may be present as an intermediate during electrochemical CO_2 reduction to hydrocarbons on copper cathodes. Evidence for CO type species as intermediates in this overall reaction came from the experimental observation that CO is electrochemically reduced both in gas phase and aqueous 0.5 M $KHCO_3$ electrolytic cells, to give similar gaseous hydrocarbon reaction products.

Because of the above observations and the fact that CO is isoelectronic with N_2, we became interested in the possibility of direct electrochemical nitrogen fixation under ambient conditions in the gas phase using solid polymer electrolyte type cells. In heterogeneous gas phase catalysis there exist several similarities between sites necessary for promoting hydrogenation of N_2 and CO to respec-

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tively NH_3 and CH_4. For example, CO can be hydrogenated to CH_4 at 450 °C using Co, Ru, Fe, Ni and Rh sites [5], whereas N_2 can be hydrogenated to NH_3 at 1 atm and 250 °C at low conversion efficiencies [6,7] using Ru, Os, Fe, Rh, Co and Ni sites. In both cases, the proposed hydrogenation path may be expected to involve initial dissociative adsorption of the precursor molecule on the catalyst site prior to its subsequent hydrogenation. From this work [6] highest activity for N_2 hydrogenation to NH_3 was found using 5 weight percent Ru supported on potassium promoted activated carbon.

We wish to report some recent work which has demonstrated the direct gas phase electrochemical reduction of N_2 to NH_3 at ambient temperature and pressure in the cell

N_2, Ru/Nafion 417/Pt, Ar(90%), H_2(10%).

2. Experimental

Nafion 417 (equiv.wt. = 1100, H^+ ion form, 0.017 in. thick) was initially boiled for 1 hr in 6M H_2SO_4 followed by similar treatment in distilled water. Electroless deposition of Ru and Cu from respectively 0.01 M solutions of $RuCl_3$ and $CuSO_4$ onto the SPE was performed using 1 M NaOH/1 M $NaBH_4$ solutions as reducing agents introduced onto the opposite side of the SPE. Metal deposition times were generally < 3 hr. Following this the SPE was reversed and Pt deposited onto its uncoated SPE side using a similar procedure, from 0.01 M H_2PtCl_6. Current collection from each electrode on the SPE was via Pt wire. N_2 (prepurified grade, Matheson) introduced into the cathode compartment of these cells, was initially passed through two c.HCl (36 weight percent) washes followed by sparging through 6 M KOH. N_2 flow rate during electrolysis was typically 20 mL/min. A 90% Ar, 10% H_2 mixture was used in the anode compartment. Gases introduced into the respective electrode compartments were initially sparged through distilled water for prehumidification to avoid drying of the SPE. Gaseous reactants leaving the cathode chamber were sparged through a 10 mL 1 M HCl trap at 0 °C. 1 mL aliquot samples from this trap were analyzed for NH_3 via an adaptation of the Berthelot reaction [8]. This was performed using two reagent solutions. The first contained 50 g phenol and 0.25 g sodium nitroferricyanide in 500 mL of distilled water. The second contained 25 g NaOH and 40 mL of a 6% sodium hypochlorite solution in 500 mL distilled water. Trap samples (1 mL) suspected of containing NH_3 were added to 1 mL of the first solution above, followed after stirring by addition of 1 mL of the second solution. In the presence of NH_3 a blue color developed over 1 hr, possessing a maximum absorbance of 630 nm. Ammonia yields were obtained from a standard absorbance curve from a known NH_4Cl solution.

3. Results and discussion

The electrochemical cell was based upon the use of the proton conducting perfluorinated sulfonic acid solid polymer electrolyte (SPE) Nafion, which acted to separate the gas phase anode compartment where hydrogen oxidation occurred at a Pt/SPE interface from the cathode compartment where N_2 reduction proceeded at the Ru/SPE interface. A schematic of the cell arrangement used in this work is shown in fig. 1.

In this work Cu/SPE interfaces were not found active for gas phase N_2 reduction. For Ru containing SPE cells, constant current electrolyses were typically performed at current densities between 0.5 and 40 mA/cm^2 where the Ru/SPE electrode potential typically varied between -0.5 and -2.5 V vs. the Pt/H_2 anode compartment. Preliminary results from this unoptimized cell are shown in table 1. Ammonia could only be detected between the current densities 1 and 5 mA/cm^2. We assume here that the major product was hydrogen since Ru is known to be an efficient electrocatalyst for hydrogen evolution. The absence of detectable ammonia under open-circuit conditions suggests ammonia synthesis here as electrochemically driven. Faradaic conversion of N_2 to NH_3 was found to be 0.0015% at 3.12 mA/cm^2 corresponding to 1.75×10^{-9} moles $cm^{-2}h^{-1}$ (on a 9.65 cm^2 electrode). These rates compare to 1×10^{-8} moles cm^{-2} h^{-1} reported during photoelectrochemical (PEC) N_2 reduction at illuminated u-Fe_2O_3 dispersions [9]. Substitution of N_2 by Ar in the cathode chamber of these cells gave no detectable ammonia, suggesting introduced N_2 as the source used during NH_3

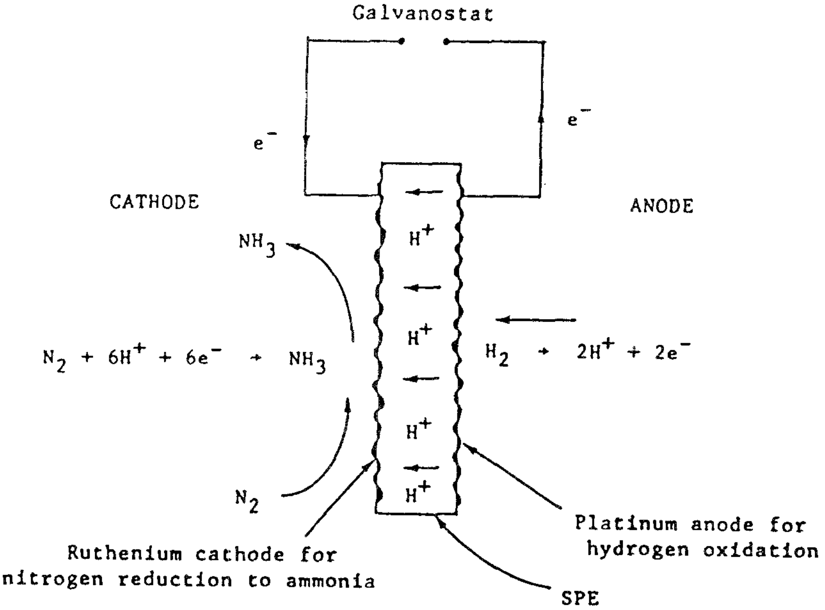

Fig. 1. Schematic of SPE cell used here for the electrochemical reduction of nitrogen.

Table 1
Faradaic efficiencies for ammonia formation from N_2 on Ru electrodes in the cell N_2, Ru/Nafion 417/Pt, Ar(90%), H_2(10%).

Current density (mA/cm^2)	Faradaic efficiency (%)
2.09	0.0010
3.12	0.0015
4.2	0.0008

synthesis.

The possibility of N_2 reduction at in situ deposited Ru (from 10^{-5} M $RuCl_3$ solutions) on glassy carbon cathodes in 0.5 M K_2SO_4 ($pH \cong 5.5$) was also investigated. Initial Ru deposition proceeded under Ar at current densities between 5–45 mA/cm^2 for 3 hr. Analysis of both trap and electrolyte solutions showed an absence of NH_3.

The observation of gas phase N_2 reduction to NH_3 in this work is probably a consequence, in part, on the higher N_2 concentrations that can be accommodated at the Ru/SPE interface compared to the liquid electrolyte cells where N_2 solubility would be only 1.52 mL/100 mL H_2O. However, even in gas phase electrochemical cells the electrode coverage of N_2 is expected to be low at the ambient pressures used [10]. It may be possible to increase ammonia yields in the Ru/Nafion 417/Pt cells by increasing the N_2 pressure. Previous work [11] on the gas phase PEC reduction of N_2, H_2O to ammonia in the gas phase in illuminated TiO_2 doped with 20% Fe_2O_3 has shown that ammonia yields increase from 1.53 μmoles at 0.3 atm N_2 to 6.95 μmoles at 1.5 atm N_2.

Future work will emphasize identification of ruthenium containing substrates which increase N_2 dissociative adsorption coverage prior to the Faradaic hydrogenation reaction.

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