Electroreduction Behavior of Dinitrogen over Ruthenium Cathodic Catalyst

Shu-Yong Zhang,* Xiu-Yun Zhang, Zuo-Shan Zhang, Yan Kong, and Shou-Nan Hua
School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, P. R. China

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Dinitrogen was reduced electrochemically at ambient temperature and pressure in aqueous solution over ruthenium catalyst. It was found that the chemically deposited ruthenium loaded on active carbon was an effective catalyst with good activity and stability for nitrogen reduction. A peak with many shoulders corresponding to the reduction of dinitrogen to ammonia was first observed in the difference linear sweep voltammogram.

To synthesize ammonia at ambient temperature and pressure especially in aqueous solution is of great importance for elucidating the mechanism of biological nitrogen fixation in nitrogenase and creating possible alternatives to the Haber–Bosch process. With Fe-protein serving as conductor to supply electrons to dinitrogen coordinated to FeMo-cofactor in nitrogenase, the biological dinitrogen fixation is rather an electrochemical process than a chemical one.[1] Therefore, electrochemical synthesis of ammonia under mild conditions in aqueous solution is of great importance in simulating biological dinitrogen fixation.

In 1989, Furuya et al. reported the first electrochemical synthesis of ammonia at ambient temperature and pressure in aqueous solution over metal phthalocyanine catalyst loaded in gas-diffusion electrode.[2–4] Owing to the low activity and poor stability of the catalyst, the electrolytic cell they used could hardly attain stable state, and no electrochemical measurement could be done. Although, many efforts have been made since 1980s, the discovery of effective electrochemical catalysts for reduction of dinitrogen with good activity remains a challenging and unsolved problem.[2–9] Being sensitive to the air and water or unstable upon electrochemical oxidation or reduction, most of dinitrogen complexes are unsuitable for catalyzing electrochemical reduction of dinitrogen.[5–10] Therefore, we turned to metals for catalyst. Ruthenium, which is able to adsorb dinitrogen at ambient temperature and pressure, was first considered. Using ruthenium chemically deposited on active carbon (Ru/C) as catalyst, we successfully reduced dinitrogen at mild conditions. In this work, we are to report our recent work on electrochemical reduction of dinitrogen and some new interesting findings.

After treating with boiling 10% NaOH and 10% HNO_3, active carbon used for preparation of catalyst was washed with deionized water and then dried in a vacuum furnace at 120 °C for 2 h. Activated with Pd sol, ruthenium was chemically deposited from 40 ml solution containing 5.2 g dm^{-3} $RuCl_3 \cdot H_2O$, 5 g dm^{-3} $NaNO_2$, 40.0 ml dm^{-3} $NH_3 \cdot H_2O$ (36%) and 12.5 ml dm^{-3} N_2H_4 (40%) at 40 °C for 3 h. After deposition, the active carbon loaded with Ru was washed with deionized water until no Cl^- can be detected. Ru/C catalyst thus obtained was then dried in a vacuum furnace at 120 °C for 2 h. For preparation of Pd/C, active carbon was first immersed in Pd sol and then treated with 5% NaOH solution. The Pd/C anodic catalyst was then washed with deionized water and dried in the same way as Ru/C. The catalytic layer of the three-phase electrode was prepared with catalyst : PTFE = 1:1 following the procedure reported elsewhere.[2]

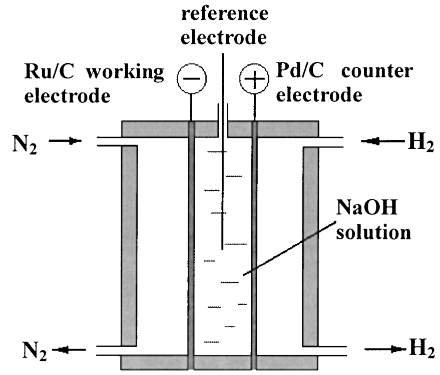

Figure 1. Schematic for the electrolytic cell for electroreduction of dinitrogen.

A conventional three-electrode cell with Ru/C cathode as working electrode, Pd/C anode as counter electrode, and Hg/HgO/NaOH (1 wt%) as reference electrode, as shown in Figure 1, was used. All potentials reported in this work refer to this reference. The exposed area of both the electrodes is 19.6 cm.^{2} A 1 wt% NaOH solution prepared with A. R. NaOH and deionized water was used as the electrolyte. Electroreduction of dinitrogen was monitored using linear sweep voltammetry (LSV) with a CHI604A electrochemical analyzer (USA). All LSV measurements were carried out between the stable potential and -1.6 V at a scan rate of 10 mV s^{-1}after the electrode attained stable state. The long-term electrolysis was conducted using a HDV-7 potentiostat (China).

As shown in Figure 2, LSV curve measured on active carbon electrode suggests the reduction of water within the potential range. Water reduction over Ru/C cathode is even more

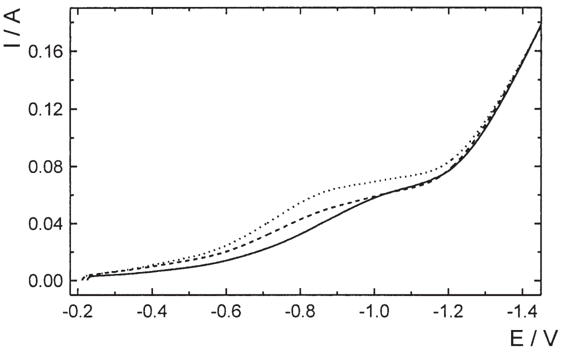

Figure 2. Linear sweep voltammograms of the carbon electrode (—), Ru/C cathode under helium (- -) or dinitrogen (. . .) at stable state.

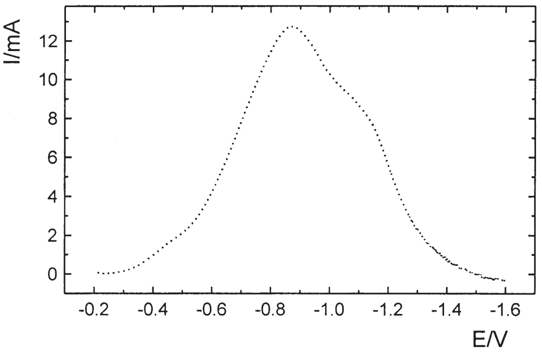

Figure 3. Difference LSV curve for electroreduction of dinitrogen over Ru catalyst.

serious than that over neat carbon. To distinguish the reduction current of dinitrogen from the total current including the reduction of water and other possible impurities and the charge of double-layer capacitor, control experiment is conducted using the same cathode under helium atmosphere.

According to Figure 2, when helium flux was switched on instead of dinitrogen, significant decrease in cathodic current can be observed. The difference curve between the LSV curves recorded under nitrogen atmosphere and helium atmosphere was depicted in Figure 3. Because any other current possibly involved in the cathode process has been subtracted, the difference LSV curve in Figure 3 is, in fact, the reduction curve for dinitrogen over Ru/C catalyst.

Being a 6-electron reduction process, the shape of the reduction peak for dinitrogen is complex as expected. Many shoulder peaks can be distinguished from the curve in Figure 3, which suggests the overlapping of some fine reduction peaks for dinitrogen.

A reduction peak with a current of 12.75 mA can be observed at -0.868 V in Figure 3, while the total cathodic current of the Ru/C cathode under dinitrogen atmosphere is 62.24 mA (cf. Figure 2). Then the current efficiency for nitrogen reduction can be estimated to be 20.48%. The low current efficiency can be mainly attributed to the hydrogen evolution reaction.

According to the reduction peak that appears in Figure 3, the long-term electrolysis was conducted by polarizing the cathode at -0.87 V. During the 20 h electrolysis, the cell voltage increased from 1.79 V to 2.00 V, while the current density decreased from 80 mA to 52 mA, which reflected the decay of reduction activity.

The exit gas from the cathode was made bubbling through a flask containing deionized water. After electrolysis, the water in the flask was tested for ammonia. It was found that the deionized water turned reddish upon the addition of phenolphthalein, and upon the addition of Nessler's reagent, formed dark yellowish precipitation. Both the experiments gave positive results for ammonia. We can, therefore, ascribe the reduction peak appearing in Figure 3 mainly to the electroreduction of dinitrogen to ammonia. Ammonia can be also detected in the electrolytic solution, which suggests the penetration of ammonia through the hydrophobic layer of the cathode.

The above results shown in Figures 2 and 3 were recorded after 6 h of electrolysis. The production rate of ammonia at this time still remains 2.64×10^{-6} mol min^{-1}, which is ca. 10 times larger than that reported by Furuya et al. only a few minutes after the very start of their experiments. This suggests that, the Ru/C catalyst is more active and more stable than the metal phthalocyanine used by Furuya et al.[2]

After 22 h of electrolysis, the current efficiency of our electrolytic cell was measured to be less than 5.6%. This means that further improvement on both activity and stability of cathodic catalyst for nitrogen reduction is still needed.

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