

Electrochemistry and Spectroscopy Study on Nitrate Reduction Catalyzed by Iron and Cobalt Protoporphyrin Immobilized Pyrolytic Graphite

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The nitrogen-cycle is one of the most important material cycles in biosphere. With the high nitrate concentration in ground water, it is important to find methods to reduce its content. Otherwise, it will be harmful for human healthy. The electrochemical reduction of nitrate is an effective technique to accomplish the goal. With iron and cobalt protoporphyrins acting as heterogenous catalyst, the nitrate ions have been reduced to hydroxylamine and ammonia efficiently. The process is highly dependent on pH as the real active reactant of the reaction is NO which comes from the disproportionation reaction of nitrite and also nitrate concentration. The detailed investigations on the influence of pH and nitrate concentration on the electrochemical reduction of nitrate on cobalt protoporphyrin illustrate that the formation of ammonia probably goes through two different pathways, one of which is a direct pathway without going through hydroxylamine and the other is a sequential pathway which is from hydroxylamine reduction. FTIR spectra confirm that the most valuable intermediate of the reaction is adsorbed HNO (M-HNO).

Keywords: Nitrate reduction; pH dependent; NO; M-HNO

1. INTRODUCTION

The use of nitrogen fertilizer has greatly improved the fertility of soil, but its extensive utilization also introduces serious environmental problems, such as the high concentration of nitrate in water[1]. As the nitrogen content increased in water, it will not only destroy the ecosystem but also cause serious damage to human body. The long-term intake of excessive nitrate will lead to mental decline, the auditory and visual reflexes relatively slow[2]. Besides, the excessvie intaking of nitrate

will cause kinds of diseases, such as high blood pressure[3], thyroid disorder[4], gastric cancer[5] and congenital malformation[6].

Therefore, it is important to reduce the nitrate concentration in water to avoid environmental and health problems. At present, there are different techniques to remove nitrate from water, such as ion exchange[7,8], reverse osmosis[9], electrodialysis, biological denitrification[10] and catalytic reduction[11]. The electrochemical reduction of nitrate combines electrochemical and catalytic techniques becoming a more effective, economic and competitive technique. Owing to its simple equipment requirements, small footprint, lack of secondary pollution and easy to achieve industrialization, the electrochemical denitrification is called as an environment-friendly technique[12-15]. However, various kinds of products could be produced from the electrochemical reduction of nitrate, such as nitrogen dioxide, nitrite, nitrous acid, nitric oxide, nitrous oxide, nitrogen, hydroxylamine and ammonia, making its limitation to be industrialized[16-19]. Therefore, various catalysts have been utilized to improve the activity and selectivity of the reaction.

In order to improve the efficiency of the reaction, different kinds of catalysts have been utilized to catalyze the nitrate electrochemical reduction. At first various noble and transition metals were investigated, such as Pt[20], Cu[21], Ag[22], Rh[23], Sn[24]. Metal alloys were also studied extensively such as CuPt[25] and PdRh1.5/Ti[26]. A relatively high N₂ selectivity with Pt-Cu and Sn cathode has been reported by de Voors et al. and Katsounaros et al. respectively[27,28]. Metal complexes are the other kinds of catalysts that are efficient to catalyze the electrochemical reduction of nitrate. Metal porphyrins[29,30], cyclams[31] and phthalocyanines[32] are the mostly investigated catalysts. The advantage of metal complexes is that they can be immobilized on the surface of electrode to accomplish the heterogeneous catalysis. However, no matter what kind of catalyst is used, the mechanism of the reaction is not clear yet.

Herein, the mechanism of the electrochemical reduction of nitrate on immobilized cobalt protoporphyrins has been exploited using electrochemical techniques, ion chromatography, and especially FTIR spectroscopy. The metal center of the catalyst makes difference on the selectivity of the ammonia formation. pH plays significant influence on the activity and selectivity too, while nitrate concentration is the other factor affecting the process in acidic solution. The possible mechanism has been discussed in order to fully understand the reaction.

2. EXPERIMENTAL

All the electrochemical experiments were conducted in a home-made one-compartment cell, which is equipped with a reversible hydrogen electrode (RHE) as a reference electrode, which all potentials in this paper refer to, a coiled platinum wire as counter electrode and a home-made pyrolytic graphite with a diameter of 5 mm as a working electrode. Prior the electrochemical measurements, all glassware has been boiled in concentrated sulfuric and nitrate acid, then boiled in Milli-Q water for 5 times. Cobalt(III) protoporphyrin IX chloride (Frontier Science) and Hemin (Frontier Science) immobilized pyrolytic graphite electrode was prepared as following: 8 mg cobalt/iron protoporphyrin was diluted in 25 mL 0.01 M borate solution, which was adjusted to pH=10 using NaOH. Then the

pyrolytic graphite electrode which was first braded with P500 and P1000 sandpaper sequentially and ultrasonicated in water for 1 min has been immersed into the solution for 5 min, after which it was rinsed with Mini Q water thoroughly before moving to cell for the following measurements. The abbreviations of PG-HER, FePP-HER and CoPP-HER represent hydrogen evolution reaction conducted on blank pyrolytic graphite, iron and cobalt protoporphyrin immobilized pyrolytic graphite electrode respectively, while PG-NRR, FePP-NRR and CoPP-NRR indicate the nitrate reduction reaction on blank pyrolytic graphite, iron and cobalt protoporphyrin immobilized pyrolytic graphite electrode respectively.

The liquid products were detected using the online ion chromatography (IC). A Teflon tip was positioned close to the surface of the working electrode to collect samples per minute through an automatic fraction collector (FRC-10A, Schimadzu). A linear voltammogram was conducted using an Autolab potentialostat (Pgstat20) from 0 V to -1.5 V vs RHE scanning in a rate of 1 mV s⁻¹. Collected samples were stored in a microtiter, which was then put onto the autosampler (SIL-20A) holder of an ion chromatography unit (Schimadzu, Prominence) equipped with a conductivity detector (CCD-10Ap). In order to monitor NH₄⁺ and NH₃OH⁺ cations, 20 μL of each sample was injected into and analyzed through two series of Shodex IC Y-521 columns. The temperature of columns was kept at 30 °C. The eluent solution was 2.5 mM nitric acid solution (Merck, Suprapur, 65%) with a flow rate of 8 mL/min.

FTIR measurements were conducted with a Bruker Vertex 80 V infrared spectrophotometer. A 60° CaF₂ prism was used as a holder on which the electrochemical cell was assembled. The working electrode was positioned against the prism. FTIR spectra exhibited were averaged from 100 scans with a resolution of 8 cm⁻¹ at potentials with 0.1 V intervals. The final spectra were shown in the form of (R-R₀)/R₀, where R is the reflectance at the sample potential and R₀ is the reflectance at the reference potential, which is 0.9 V in this case. Therefore, the bands pointed up presented for the formation of species, while the bands pointed down stood for the consumption of species.

3. RESULTS AND DISCUSSION

Cyclic voltammetry (CV) is a powerful technique to exploit the catalytic activity of catalysts in a full picture. Therefore, cyclic voltammograms of the hydrogen evolution reaction (HER) and nitrate reduction reaction (NRR) have first been compared on blank pyrolytic graphite electrode and metal protoporphyrins immobilized electrode in 0.1 M HNO₃ solution (pH=1) as shown in Figure 1. As for blank pyrolytic graphite electrode, the onset potential for the hydrogen evolution reaction is around -0.75 V, which indicates that the process needs high energy input to be initiated. While in 0.1 M HNO₃ solution, the onset potential for the nitrate reduction reaction is a little more negative than that for HER. This is probably because that nitrate reduction is more difficult on pyrolytic graphite. Besides, the highest current density at -1.5 V in 0.1 M HNO₃ solution is more positive than that in 0.1 M HClO₄ solution, indicating that nitrate ions may absorb on the surface of pyrolytic graphite electrode blocking the active sites for HER. As iron protoporphyrin immobilized on the pyrolytic graphite, the onset potential for HER is even more negative than that on blank pyrolytic graphite, suggesting that hemin is

not catalytic active for HER. However, the onset potential of NRR on hemin immobilized pyrolytic graphite electrode is a bit more positive than that of HER and the highest current density of NRR is higher than that of HER, indicating that iron protoporphyrin is catalytic active for NRR. When the pyrolytic graphite immobilized with cobalt protoporphyrin, the onset potential for both HER and NRR is much more positive than on blank pyrolytic graphite and iron protoporphyrin immobilized electrode, illustrating that cobalt protoporphyrin is much more catalytic active. Furthermore, the onset potential and the current density in 0.1 M HNO₃ and HClO₄ solution does not exist big discrepancy, suggesting that HER is the domain reaction on cobalt protoporphyrin immobilized electrode at pH=1. On summary, no matter on which electrode discussed here, HER is dominated at pH=1. It is hard to compare the activity of them only by cyclic voltammograms. Therefore, other techniques have been utilized to investigate the process as following.

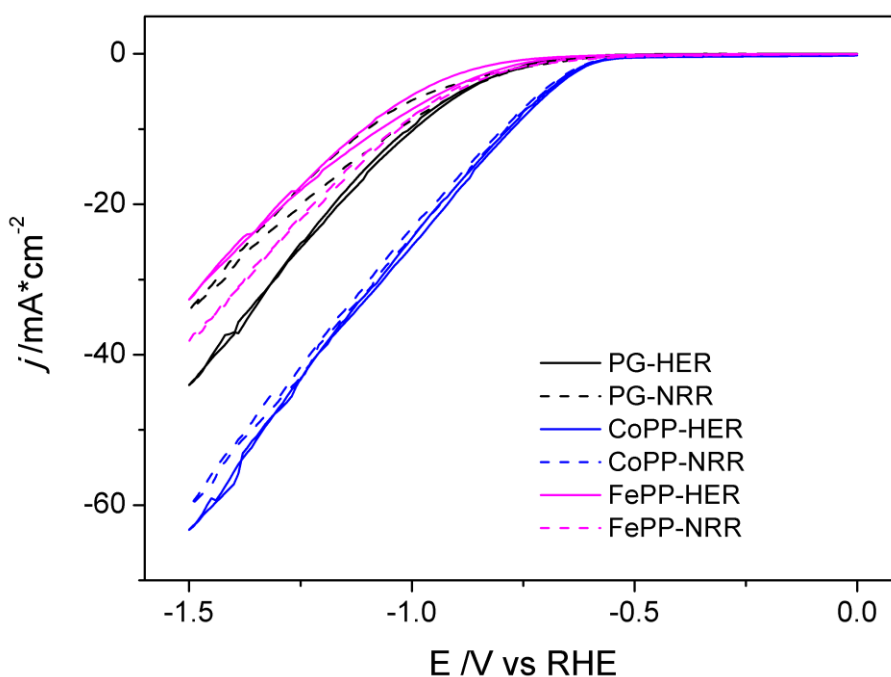


Figure 1. The cyclic voltammograms of reactions in 0.1 M HNO₃ or HClO₄ solutions at a scan rate of 100 mV/s in a potential range from 0 to -1.5 V vs RHE. Black solid line: hydrogen evolution reaction on blank pyrolytic graphite electrode; Black dashed line: nitrate reduction reaction on blank pyrolytic graphite electrode; Blue solid line: hydrogen evolution reaction on cobalt protoporphyrin immobilized pyrolytic graphite electrode; Blue dashed line: nitrate reduction reaction on cobalt protoporphyrin immobilized pyrolytic graphite electrode; Purple solid line: hydrogen evolution reaction on iron protoporphyrin immobilized pyrolytic graphite electrode; Purple dashed line: nitrate reduction reaction on iron protoporphyrin immobilized pyrolytic graphite electrode.

As illustrated in literature, NRR is a process highly dependent on pH. Then, it makes sense to also investigate HER and NRR on blank pyrolytic graphite and metal protoporphyrins immobilized pyrolytic graphite at different pH using cyclic voltammetry. The results at pH=2 is similar as those at

pH=1. Therefore, only the results at pH=3 have been shown in Figure 2. Compared with voltammograms obtained at pH=1, the most remarkable difference is that the onset potential of HER on both blank pyrolytic graphite electrode and metal protoporphyrins immobilized electrode is much more negative at pH=3, indicating the difficulty of HER. This was illustrated that HER resulted from the direct reduction of H^+ at pH=1, while water is reduced at pH=3. Even though the onset potential is more negative on all investigated electrodes at pH=3 than that at pH=1, iron and cobalt protoporphyrin still present catalytic active towards HER as compared to the reactions on blank pyrolytic graphite. As for NRR, both iron and cobalt protoporphyrin immobilization makes the onset potential move to positive direction suggesting their catalytic activity towards the reaction. On the other hands, the onset potential for NRR is the most positive on the iron immobilized electrode, probably resulted from the higher catalytic activity of it. On iron immobilized electrode, the voltammogram in $NaNO_3$ solution presents a cathodic peak around -1.2 V which is probably related to the reduction of nitrate ions indicating the high catalytic capability of iron protoporphyrin. The current density on all investigated electrodes at pH=1 is several folds less than that at pH=1. This is mainly because that HER is highly suppressed at pH=3. The cyclic voltammetry gives first full information of the active reactions occurred on the investigated electrodes. However, in order to further understand products distribution, the ionic chromatography has been utilized to investigate the system.

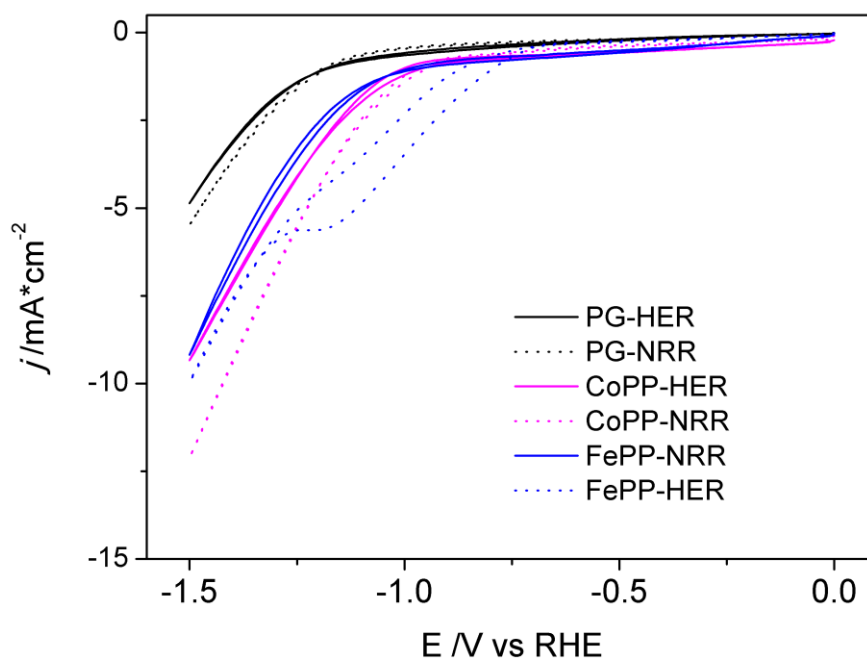


Figure 2. The cyclic voltammograms of reactions in 0.001 M $HClO_4$ + 0.099 M $NaNO_3$ (NRR) or 0.001 M $HClO_4$ + 0.099 M $NaClO_4$ (HER) solutions at a scan rate of 100 mV/s from 0 to -1.5 V. Black solid line: hydrogen evolution reaction on blank pyrolytic graphite electrode; Black dashed line: nitrate reduction reaction on blank pyrolytic graphite electrode; Purple solid line: hydrogen evolution reaction on cobalt protoporphyrin immobilized pyrolytic graphite electrode; Purple dashed line: nitrate reduction reaction on cobalt protoporphyrin immobilized pyrolytic graphite electrode; Blue solid line: hydrogen evolution reaction on iron protoporphyrin immobilized pyrolytic graphite electrode; Blue dashed line: nitrate reduction reaction on iron protoporphyrin immobilized pyrolytic graphite electrode.

The catalytic activity and product distribution has been verified using ionic chromatography at pH=1 as shown in Figure 3. The main products obtained from nitrate reduction on blank pyrolytic graphite electrode and metal protoporphyrins immobilized electrodes are ammonia (NH_4^+) and hydroxylamine (NH_3OH^+). On the blank pyrolytic graphite electrode, the concentration of both ammonia and hydroxylamine is lower than 0.2 mM, manifesting that blank pyrolytic graphite is not with high catalytic activity towards NRR. Besides, the onset potential for the formation of both ammonia and hydroxylamine is around -0.9 V, resulted from the low catalytic capability of the electrode. With iron or cobalt protoporphyrin immobilized on the pyrolytic graphite electrode, the concentration of ammonia and hydroxylamine produced from NRR has dramatically increased. The highest concentration of hydroxylamine produced on iron and cobalt protoporphyrin immobilized electrode both reaches to 0.7 mM at the potential around -1.5 V. It is also could be found that the onset potential for the hydroxylamin formation on both catalysts is almost the same, around -0.5 V. However, the formation of ammonia is quite different between iron and cobalt protoporphyrin immobilized electrode. On iron protoporphyrin immobilized electrode, ammonia is initiated to be produced at about -0.9 V, while the concentration is increased quickly with the potential scanned to negative direction and reaches the maximum of 0.7 mM at -1.35 V. With the potetial further scanned to more negative, the concentration of ammonia is decreased.

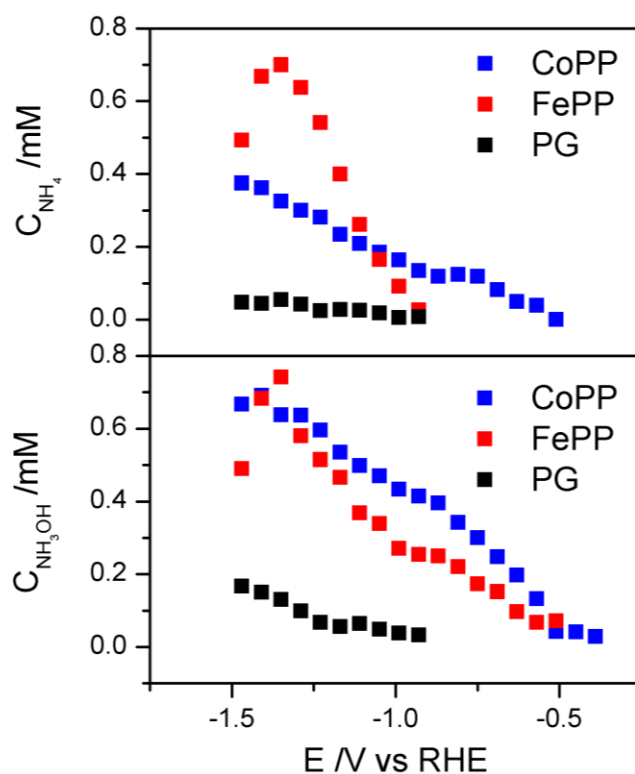


Figure 3. Plots showing the concentration of NH_3OH^+ and NH_4^+ as a function of potential from the electrochemical reduction of nitrate at pH=1 on the cobalt (■) or iron (■) protoporphyrins immobilized and blank (■) pyrolytic graphite electrode.

On the other hand, the ammonia starts being produced at relatively more positive potential, about -0.5 V on cobalt protoporphyrin immobilized electrode. With the potential becoming more and more negative, the ammonia has been formed gradually and reached the highest concentration of 0.37 mM at -1.5 V. The difference of the ammonia formation on iron and cobalt protoporphyrin immobilized electrode illustrates that the pathway for the formation of ammonia is different on those two catalysts indicating that the metal center is essential for the ammonia formation, while the formation of hydroxylamine is not as sensitive to metal center as ammonia. The same experiments have been also conducted at pH=2 and pH=3, the results on cobalt protoporphyrin immobilized electrode were exhibited in our previous work[33]. With pH increasing slightly, the concentration of hydroxylamine and ammonia formed from the electrochemical reduction of nitrate has dramatically decreased. When pH reaches 3, the formation of hydroxylamine and ammonia can hardly be detected. The results on iron protoporphyrin immobilized electrode are almost the same as on cobalt protoporphyrin. Therefore, the concentration profile of hydroxylamine and ammonia as a function of potential from the nitrate reduction is not presented here.

The influence of nitrate concentration on the catalytic activity is investigated using on-line ion chromatography as shown in Figure 4. At pH=1, it is clear that the concentration of nitrate is essential for the NH_3OH^+ and NH_4^+ formation from the nitrate reduction. The concentration of NH_3OH^+ and NH_4^+ reaches 0.7 and 0.38 mM respectively in 0.1 M HNO_3 electrolyte. While the concentration of nitrate reduces one magnitude to 10 mM, the formation of NH_3OH^+ and NH_4^+ is greatly suppressed 0.2 mM and 0.05 mM respectively. The onset potential for the formation of NH_3OH^+ and NH_4^+ is at -0.7 V and -1.2 V in 10 mM nitrate solution respectively, while it is -0.35 V and -0.5 V in 0.1 M nitrate solution respectively. This indicates the low catalytic activity of cobalt protoporphyrin with the increasing of nitrate concentration. In acidic electrolyte, nitrate concentration is an important factor affecting the formation of hydroxylamine and ammonia. As pH increases to 6.5, pH becomes the most important factor for the nitrate reduction to NH_3OH^+ and NH_4^+ instead of nitrate concentration as shown in Figure 4. Only a tiny amount of NH_3OH^+ and NH_4^+ which is with a highest concentration of 0.062 and 0.06 mM respectively could be detected at pH=6.5. On the contrary to the situation at pH = 1, the onset potential for the formation of both NH_3OH^+ and NH_4^+ is more negative with a nitrate concentration of 0.1 M indicating that it is more difficult to reduce nitrate with higher nitrate concentration. On the other hand, the concentration of NH_3OH^+ is almost the same at both nitrate concentration at pH=6.5, while the concentration of NH_4^+ in 0.1 M nitrate solution is about 3 time higher than that in 10 mM electrolyte. From which we can deduce that the formation of NH_4^+ is more sensitive to the nitrate concentration compared to NH_3OH^+ production.

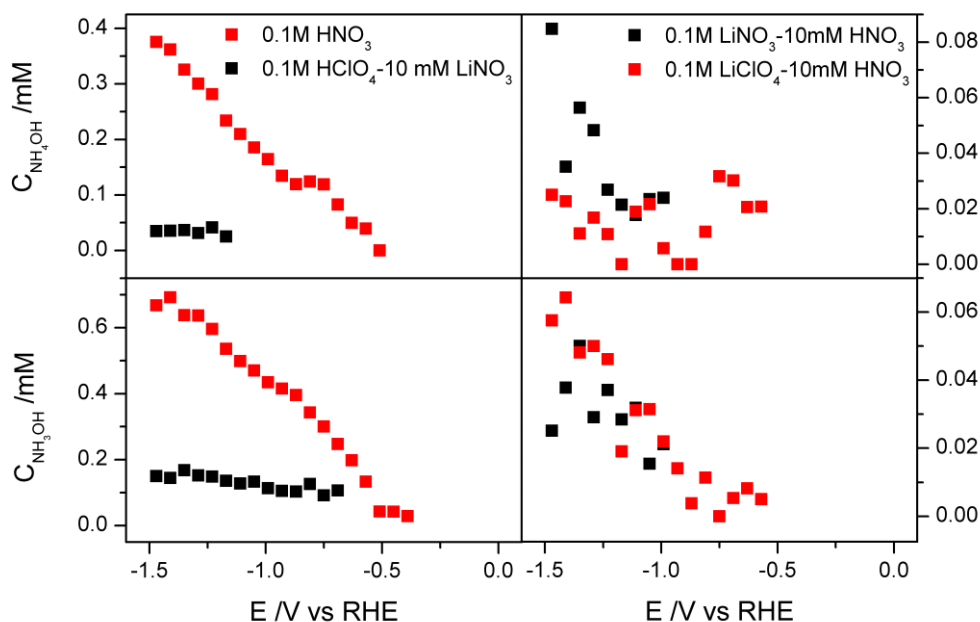


Figure 4. Plots showing the concentration of NH_3OH^+ and NH_4^+ as a function of potential from the electrochemical reduction of nitrate on cobalt protoporphyrin with 0.1 M (■) or 0.01 M (■) nitrate concentration at pH=1 (left side) and pH=3 (right side).

As discussed above, the formation of ammonia is more sensitive to the metal center and nitrate concentration compared to hydroxylamine formation indicating that the formation of hydroxylamine and ammonia possibly undergoes different pathway. In order to fully understand the process of the electrochemical reduction of nitrate, it is necessary to study the formation of ammonia in detail. The most probable precursor for the ammonia formation is hydroxylamine. Therefore, the electrochemical reduction of hydroxylamine on cobalt protoporphyrin immobilized pyrolytic graphite electrode at different pH has been investigated as shown in Figure 5. From Figure 5, it can be find out that the concentration of hydroxylamine is decreased with increasing of pH even with the same initial concentration. This could probably because that the signal detected from ionic chromatography is protonated hydroxylamine making the lower concentration of protonated hydroxylamine at higer pH. Besides, it is clear that the concentration of ammonia produced from the electrochemical redcution of hydroxylamine is increased with pH increasing indicating that the process prefers to alkaline media. On the other hand, the concentration of hydroxylamine is decreasing as soon as the formation of ammonia elucidating that hydroxylamine is exactly the precursor of the ammonia formation. Furthermore, the pH dependence trend of ammonia formation is oppsite from the nitrate reduction and hydroxylamine reduction. From our previous work[33], the concentration of ammonia produced from the nitrite reduction is higher at pH=2 than that at pH=1. This may result from the compamise of different pH sensitivity between the electrochemical reduction of nitrite and hydroxylamine. It makes sense to speculate that the higher concentration of ammonia formed at pH=1 from the nitrate reduction probalby results from a direct reduction pathway of nitrate which does not go through hydroxylamine as an intermediate. Therefore, we can conclude that the formation of ammonia from nitrate reduction probably undergoes a direct pathway without hydroxylamine as an intermediate. Chebotarea claimed

that ammonia is the main product from the electrochemical reduction of nitrite and nitrate on metal phthalocyanine[34] which is a similar complex as porphyrin. But hydroxylamine is only obtained on reduction of NO_2^- . This is indirectly consistent with our conclusion which nitrate could be reduced to ammonia directly without nitrite as intermediate. Besides, de Groot reported that hydroxylamine has been produced on hemin immobilized pyrolytic graphite with 100% selectivity from the electrochemical reduction of NO [35]. This can further confirm that ammonia produced from nitrate reduction should follow a pathway without going through NO as an intermediate.

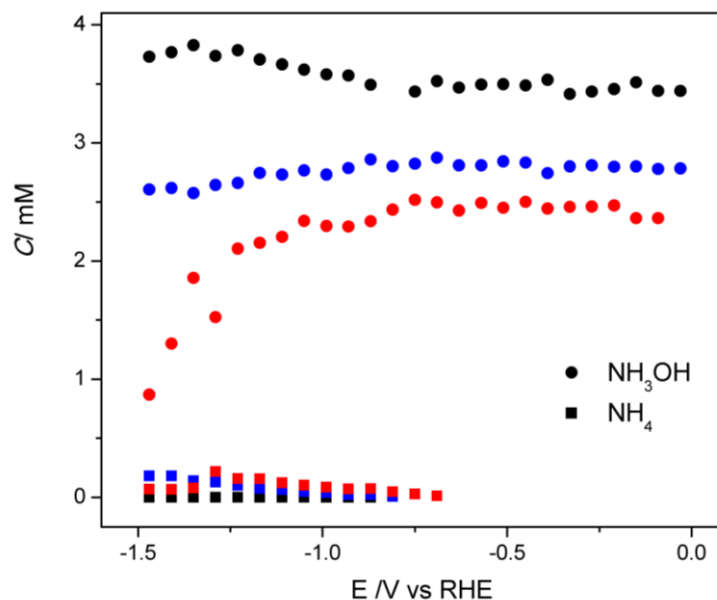


Figure 5 Plots showing the concentration of NH_3OH^+ (●) and NH_4^+ (■) as a function of potential from the electrochemical reduction of hydroxylamine on cobalt protoporphyrin immobilized pyrolytic graphite electrode at pH = 1 (black), pH = 2 (blue) and pH = 3 (red)

The nitrate electrochemical reduction is highly dependent on pH and the rate determining step is the first two-electron transferring converting nitrate to nitrite (as shown in equation 1). In acidic solution, NO is produced from decomposition reaction of HNO_2 as presented in equation 2 and 3. The NO adduct which is confirmed using spectroscopic study as presented following is then produced through equation 4.



The NO adduct is considered to act as the precursor which is further reduced to final products through proton-coupled electron transfer reactions. In order to completely understand the mechanism of the electrochemical reduction of nitrate on cobalt protoporphyrin, the Frontier Transfer Infra-red spectroscopy (FTIR) has been utilized to exploit the possible intermediates during the reaction as shown in Figure 6. The first band, at 1712 cm^{-1} , corresponds to the N-O stretching of NO adsorbed. The

peak pointing down indicates the consuming of NO during the measurements. This probably illustrates that NO is the actual reactant of the reaction. The bands located at 1570 and 1470 cm^{-1} probably correspond to N-O stretching of NO_2 which is either a by-product of nitrate reduction or comes from the disproportionation of HNO_2 as shown in the equation (3). However, Younathan team investigated the electrocatalytic reduction of nitrite and nitrosyl by iron(III) protoporphyrin IX dimethyl ester and found that the formation of NO_2 is one possible pathway from twice-reduced intermediate, $[\text{Fe}^{\text{II}}(\text{NO}^-)(\text{PP})]$ [36]. There has another peak located at 1395 cm^{-1} which probably represents to the N-O stretching of HNO, which is the intermediate following the adsorption of NO molecule. This step is consistent with de Groot's speculation that the rate-determining step in the electrochemical reduction of NO on hemin immobilized electrode is comprised of an electron-proton coupled transfer[35]. Furthermore, nitrite has been considered to coordinate to the metal center of metal porphyrins[37, 38]. However, the characteristic peaks related to nitrite adsorption are not discovered here. Based on the FTIR results, it could be concluded that the actual active reactant of the nitrate reduction is NO. This can explain why the electrochemical reduction of nitrate is highly pH dependent as the formation of NO requires protons.

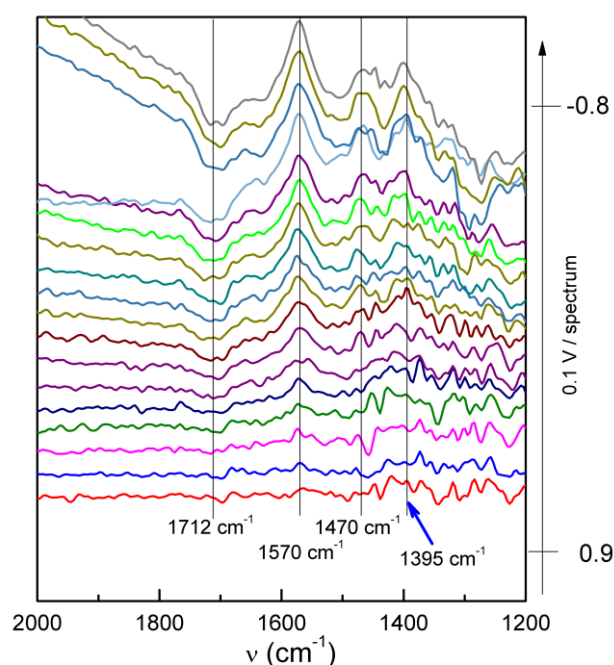


Figure 6 Potential dependent absorbance spectra for nitrate reduction on cobalt protoporphyrin immobilized PG electrode in 0.1 M HNO_3 solution. Reference spectrum recorded at +0.9 V vs. RHE. Highlighted bands and their corresponding frequencies are indicated with a vertical line.

As illustrated in equations (1) to (3), nitrate is first electrochemically transferred to nitrite which is then chemically reacted into NO. These three steps require highly acidic condition leading to the pH dependence of the nitrate reduction. As long as NO is formed in the solution, it will adsorb on the metal center of metal protoporphyrin to form M-NO intermediate as shown in equation (4). The adsorbed M-NO will go through an electron-proton coupled process to form N-HNO intermediate which will be further reduced till the final products. However, the FTIR results could not reveal the

other possible intermediates after M-HNO intermediate is formed making that it is difficult to monitor steps further.

4. CONCLUSIONS

As illustrated above, cobalt and iron protoporphyrins are catalytically active towards the electrochemical reduction of nitrate, while cobalt protoporphyrin exhibits a higher ratio of hydroxylamine to ammonia. The investigation on the mechanism of the nitrate electrochemical reduction indicates that the reaction is highly dependent on pH and nitrate concentration. The formation of ammonia probably goes through two different pathways, one of which is a sequential pathway through hydroxylamine to final product, while the other is a direct pathway which produces ammonia directly from nitrate. FTIR results demonstrate that NO_2 is either a possible by-product from the reaction or the product of disproportionation reaction of HNO_2 which is from chemical reaction of nitrite in acidic solution. Besides, it can be concluded that NO is the actual effective reactant and the adsorbed NO will further be reduced to form M-HNO which is the key intermediate of the formation of hydroxylamine and ammonia. Even though it is not clear about the steps after M-HNO formation and how it performs the direct pathway yet. It is still worthy to find out the real reactant, the cause of the pH dependence and the key intermediate of the sequential pathway.

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