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pH dependence of the electroreduction of nitrate on Rh and Pt polycrystalline electrodes

Abstract

In this Chapter, the reduction of nitrate is investigated on Rh and Pt polycrystalline electrodes over a wide pH range. In acid media, the Rh electrode shows a higher activity for nitrate reduction than the Pt electrode, but the activity of nitrate reduction generally decreases as solution pH increases, on both electrodes. However, there is no activity for nitrate reduction on Pt electrode for $\text{pH} > 5$, whereas a certain pH-independent constant activity is still observed on Rh electrode for $\text{pH} > 5$. Relating the activity of nitrate reduction to the nitrate states (HNO_3 , NO_3^-) in solution as a function of pH, it is suggested that HNO_3 is the only reducible species for nitrate reduction on Pt, whereas both HNO_3 and the nitrate anion are reducible species on Rh, so that a significant activity of nitrate reduction is sustained on the Rh electrode above $\text{pH}=5$. This suggests that the high catalytic activity of Rh can also activate nitrate even if no free protons are available in solution.

5.1. Introduction

The electrochemical reduction of nitrate has been paid considerable attention for many decades because of the necessity to convert nitrate in wastewater to dinitrogen, that is benign to the environment,¹ but also because of the opportunity to generate valuable products for the chemical industry, such as hydroxylamine and nitric oxide.²

Much research work has been devoted to transition-metal electrode materials due to their chemical nobility and specific catalytic properties. Platinum, both single crystalline and polycrystalline, is the one that is most commonly applied to study the mechanism of nitrate reduction. From various studies, nitrate reduction has been shown to depend on nitrate concentration, electrolyte acidity and electrolyte anions.²⁻⁷ Ammonia is the main (only) product of nitrate reduction on platinum in acid solution.^{5, 6, 8} However, nitrate reduction on Pt electrode is quite slow. To enhance the activity of nitrate reduction in acid, the Pt surface can be modified with another metal (Chapters 2-4), which may also lead to a specific selectivity to form a certain product.⁹⁻¹² Even though nitrate reduction has been mostly investigated in acid medium, where it is largely facilitated by availability of protons, probing the performance of nitrate reduction over a wide range of pH would be helpful to obtain a deeper understanding of the mechanism of nitrate reduction and the role of the proton donor, simultaneously with the electrocatalytic property of the electrode material. It is known that there is a low rate of nitrate reduction on Pt (100) in neutral medium¹³ and on Pd-modified Pt(100) in alkaline medium,¹⁴ but there is no evidence of nitrate reduction on polycrystalline Pt in alkaline medium, although nitrite reduction is particularly active on the Pt(100) surface, yielding ammonia and N₂ as products.^{15, 16} In contrast, rhodium shows higher activity and weaker influence of anion in acid than platinum,⁵ and ammonia was found as the main product.^{17, 18} Moreover, if Rh is alloyed with a low amount of Pt (Rh₈₀Pt₂₀), a higher nitrate reduction activity was found compared to pure Rh in sulfuric acid.¹⁹ It has been suggested that the Rh-Pt alloy can also alleviate the surface poisoning during nitrate reduction in acid.¹⁸ Interestingly, Rh shows a significant activity for nitrate reduction over a wide pH range, including alkaline media. The formation of ammonia and nitrite were found to depend on the solution pH such that ammonia formation dominates in acid medium whereas nitrite formation dominates when the solution pH is above 7.^{17, 20} However, apart from the different catalytic effects of Pt and Rh on nitrate

reduction, there is still little fundamental insight into their pH dependence. Therefore, it is important to investigate nitrate reduction in a wider pH range including a comparison between Pt and Rh electrodes, which is the topic of this Chapter.

5.2. Experimental

All experiments were carried out at room temperature and ultrapure water (Millipore MilliQ, resistivity $> 18.2 \text{ M}\Omega \text{ cm}$) was used to prepare solution. The electrochemical cell and glassware used in the experiment were cleaned in acid according to a procedure described elsewhere²¹ and then boiled with ultrapure water. NaNO_3 (Merck, 99.99%) was applied to study the nitrate reduction in different solutions. Phosphoric acid (Merck, suprapur), NaH_2PO_4 (Merck, 99.99%), Na_2HPO_4 (Merck, 99.99%) and Na_3PO_4 (Sigma-Aldrich, 99.99%) were used to prepare the phosphate buffers and the total concentration of phosphate was kept constant at 0.1 M. Perchloric acid (Merck, superapur) and NaClO_4 (Merck, suprapur) were used to prepare the perchlorate solution; sulfuric acid (Merck, suprapur) and Na_2SO_4 (Merck, suprapur) were used to prepare the sulfate solution. The total concentrations of the perchlorate and the sulfate in solution were kept at 0.1 M. NaOH (Merck, 99.99%) was used to prepare alkaline solution. The solution pH was checked by a pH meter (Radiometer, Copenhagen) before the experiment and the deviations of pH value for each repeated measurement were within 0.3 unit. Due to perchlorate reduction on Rh,²² perchlorate solution was only applied to study nitrate reduction on Pt electrode.

Polycrystalline Pt and Rh electrodes were used to study the pH effect on nitrate reduction. Before the electrochemical measurement, the Pt electrode was flame annealed and then cooled down to room temperature in Ar (Air Products, BIP Plus), whereas the Rh electrode was cooled down in the mixture of H_2 (Air Products, BIP Plus) and Ar in a ratio of 1:1 immediately after the flame-annealing. Pt wires were used as the counter electrodes and a reversible hydrogen electrode (RHE) was used as reference electrode. Dissolved oxygen was purged by bubbling Ar gas through the solution before the electrochemical measurement. All voltammograms were recorded by a potentiostat (Autolab Pgstat20).

5.3. Results and Discussion

In Figure 1 (a), the cyclic voltammograms of a polycrystalline Rh electrode are shown, recorded in phosphate solution over a broad pH range. All voltammograms shown in Figure 1 were obtained after the electrode surface was cycled at faster scan rate (50 mV/s) until a stable shape was obtained.

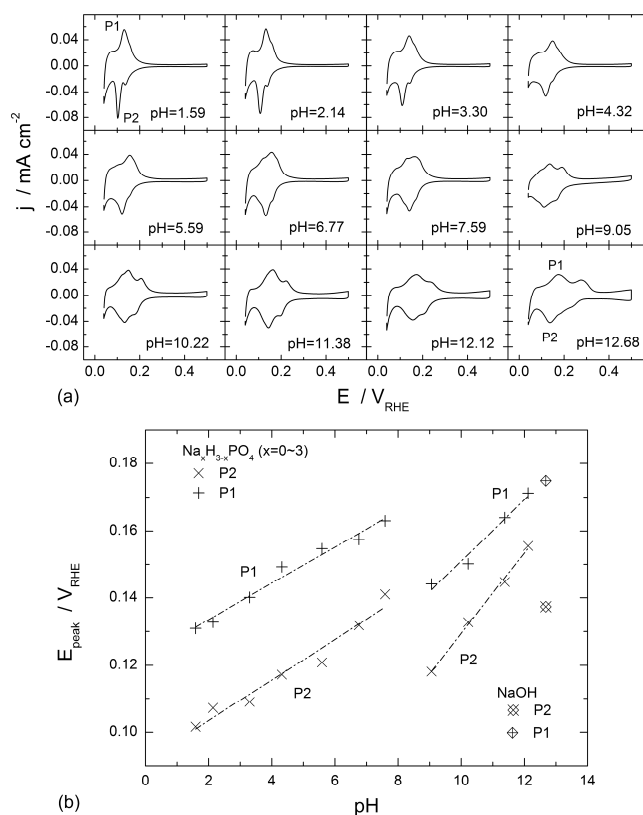


Figure 1. (a) The cyclic voltammograms of a polycrystalline Rh electrode in solutions of different pH at a scan rate of 10 mV/s and (b) the pH dependence of peak potentials of P1 and P2.

The voltammograms show two main peaks at relatively low potential ("hydrogen region"), labeled P1 and P2. These peaks presumably correspond to the desorption and adsorption of hydrogen together with anion adsorption/desorption and most likely also surface oxidation.²³ As the solution pH increases from neutral to alkaline range, an additional peak appears at more positive potential, the exact nature of which is unclear. Figure 1(b) shows that a

linear relationship between the peak potentials (on the RHE scale) and solution pH exists. The change in the peak potential (on the RHE scale) with pH is 6.1 mV pH^{-1} for peak P2 and 5.4 mV pH^{-1} for peak P1 in the pH range between 1 and 8, and 12.0 mV pH^{-1} for peak P2 and 9.2 mV pH^{-1} for peak P1 in the pH range between 9 and 13. A similar pH dependence of the peak potential corresponding to the hydrogen region (11 mV pH^{-1}) has been observed on polycrystalline Pt.²⁴ If the surface reaction corresponding to the peak would involve one proton per electron, this pH dependence should be 0 mV pH^{-1} on the RHE scale. On Pt, this pH dependence can be identified with voltammetric features corresponding to (110) and (100) surface sites,²⁵ and has been ascribed to surface reactions in which adsorbed hydrogen is replaced by adsorbed oxygen species, with the ratio of hydrogen and oxygen adsorbates depending on pH (leading to the non-zero pH dependence on the RHE scale). On Pt, it has also been established that the slope does not reflect the co-adsorption of anions,²⁵ and we will assume that the same holds for Rh, though this would really necessitate measurements in a solution free of strongly adsorbing anions.

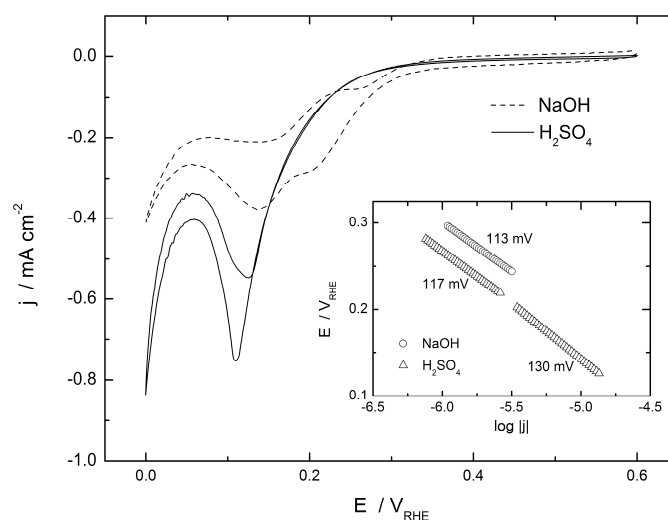


Figure 2. A comparison of nitrate reduction on a Rh polycrystalline electrode in 0.1 M H_2SO_4 and 0.1 M NaOH solution with 10 mM NaNO_3 at the scan rate of 5 mV/s. The inset shows the Tafel plot obtained from the voltammetry at 1 mV/s in the negative-going scan.

The voltammetry of nitrate reduction in 0.1 M H_2SO_4 and 0.1 M NaOH solution is compared in Figure 2. In H_2SO_4 solution, the reduction current increases

exponentially from 0.35 V in the negative-going scan and the peak potential of nitrate reduction is at around 0.1 V. The peak is most likely due to the hydrogen adsorption that competes for the active surface sites with nitrate, similar to polycrystalline Pt.⁵ Hydrogen evolution starts close to 0 V. In NaOH solution, the reduction current starts to increase at approximately the same potential as in H₂SO₄ solution, with cathodic peaks around 0.2 V and 0.14 V. These peaks correspond to the cathodic peaks in the blank solution of 0.1 M NaOH. Tafel slopes were obtained from the onset on nitrate reduction, as shown in the inset in Figure 2. For both acid and alkaline media, a similar slope of ca. 113 mV dec⁻¹ is found for potentials above 0.22 V. This indicates that the rate-determining step is independent of the solution pH.

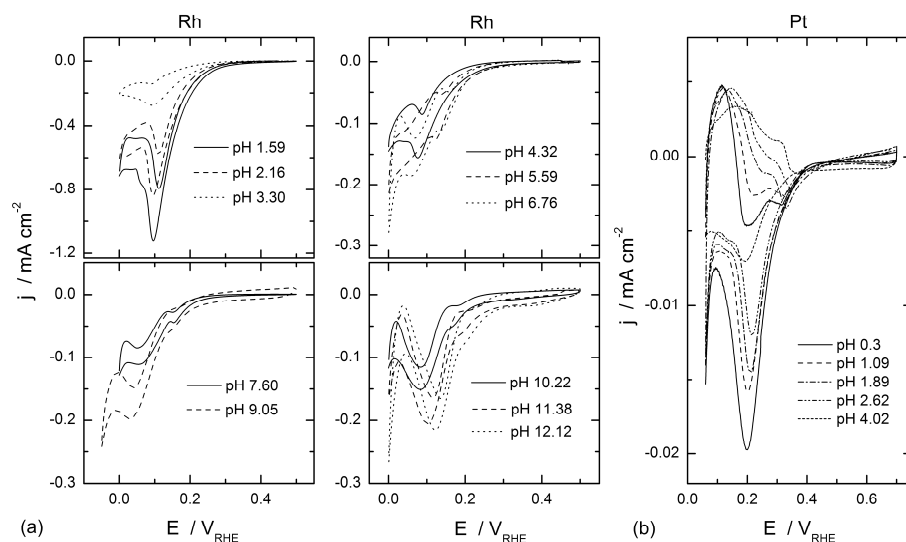


Figure 3. Cyclic voltammograms of nitrate reduction on (a) Rh polycrystalline electrode in a wide pH range of phosphate buffer solution and (b) Pt polycrystalline electrode in acidic perchlorate solution, at the scan rate of 5 mV/s.

The nitrate reduction was investigated on Rh and Pt over a wide pH range from 2 to 12 and the corresponding cyclic voltammograms are shown in Figure 3. The voltammograms of nitrate reduction on Rh show some clear changes with solution pH. In the most acidic media, the peak current decreases with increasing solution pH, and a reduction peak is not observed in solution of pH≈5.6. In neutral and alkaline media, the reduction peak recovers again and the activity of nitrate reduction increases slightly with increasing solution pH. In Figure 4, the peak-

current density and peak potential of nitrate reduction are plotted as a function of pH. The pK_a of nitric acid is about -1.3,²⁶ so that the nitrate concentration in solution is constant in whole pH range investigated (see Figure 4(c)).

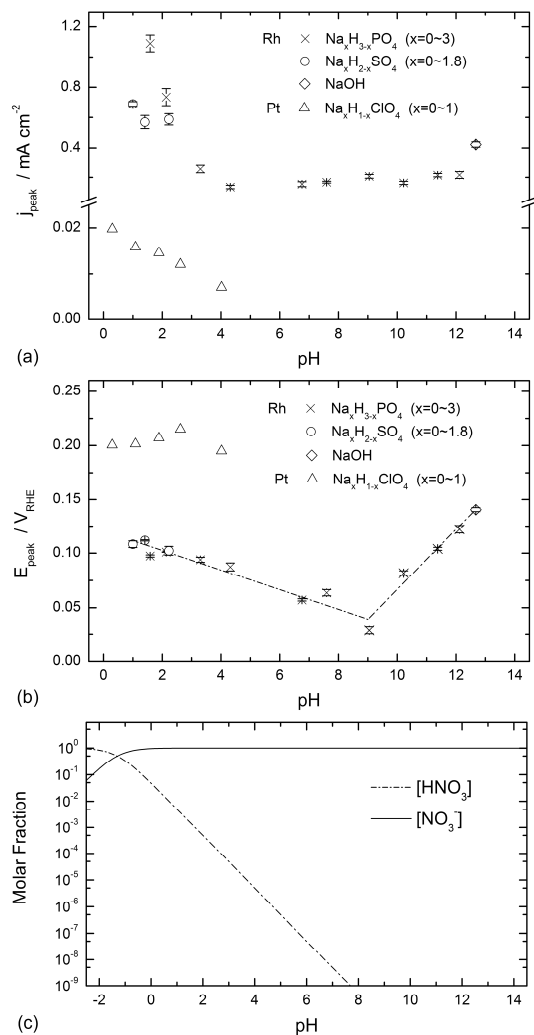
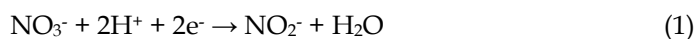


Figure 4. Variation of (a) peak current densities and (b) peak potentials for nitrate reduction on Pt and Rh electrodes over a wide pH range. The peak values were acquired from cyclic voltammetry at the scan rate of 5 mV/s. The experiments for Rh were repeated 3 times for each pH. (c) shows the molar fractions of nitrate and nitric acid as a function of the solution pH.

Nitrate reduction on Pt is also found to be strongly influenced by solution pH as the peak current density decreases with increasing pH in the acid range between pH = 0 and pH = 4 (see Figures 3 (b) and 4 (a)). For pH higher than 4, there is no observable activity for the nitrate reduction on Pt. Interestingly, Rh still shows activity in this pH range.⁵ The activity is largely pH independent above pH>4 with a slightly higher activity in 0.1 NaOH, presumably related to the absence of phosphate in this solution.

Figure 4 (b) shows how the voltammetric peak of nitrate reduction on Pt and Rh depends on solution pH. On the Pt electrode, there is no clear slope of the peak potential (i.e. constant potential). On Rh electrode, the peak shifts with a slope of 9 mV_{RHE} pH⁻¹ below pH=9 and a second distinctive region of pH dependence is observed between 10 and 13, where the slope is about - 25 ± 2 mV_{RHE} pH⁻¹, or ca. 35 ± 2 mV_{NHE} pH⁻¹, which would formally correspond to a redox reaction transferring 2 electrons per proton. Since the Tafel slope on Rh in alkaline solution is the same as in acidic solution, this pH dependence is somewhat difficult to interpret. As noted above, the peaks for nitrate reduction on Rh in alkaline solution also involve some influence of the blank voltammetry, so that it is not clear how meaningful the pH dependence of the peak potential in this pH range really is. In acidic medium, the pH dependence agrees with a concerted proton-electron transfer in the rate-determining step, as suggested by the overall reaction:



In solution there is equilibrium between nitrate and nitric acid, and their molar fractions as a function of the solution pH are shown in Figure 4 (c). The concentration of nitric acid decreases exponentially as the solution pH increases and is practically negligible (i.e. < 1 µM) for pH>5, whereas the concentration of nitrate can be considered constant for all pH>0. Relating the trend in peak current densities of nitrate reduction on Pt and Rh electrodes to the concentrations of HNO₃ and NO₃⁻ in the same pH range, we suggest the following explanation for the pH dependence of nitrate reduction. On the Pt electrode surface, the HNO₃ molecule is the only active species for nitrate reduction, whereas on Rh electrode surface both HNO₃ and NO₃⁻ are actively reducible species. As a result, the activity of nitrate reduction on a Pt electrode decreases as solution pH increases. When the solution pH is higher than 5, the concentration of HNO₃ is too low to lead to measurable activity. On the other hand, a certain constant activity of nitrate reduction is still observed on Rh electrode for pH>5, even in the absence of HNO₃,

due to the ability of Rh to activate NO_3^- . However, the HNO_3 form is considered as a more easily reducible species than NO_3^- on both Pt and Rh electrode surfaces, and therefore a much higher activity is observed in a solution of higher acidity. In such a model, the activity of nitrate reduction should peak at a pH equal to the pK_a of HNO_3 , i.e. $\text{pH}=-1.3$,^{27,28} but measurements at such high acidity are complicated, also because the indirect mechanism of nitrate reduction, that occurs in strongly acidic solution, becomes predominant.⁶

5.4. Conclusions

Nitrate reduction has been investigated on Pt and Rh polycrystalline electrodes in a broad pH range. The Rh electrode shows a considerable catalytic effect for nitrate reduction in neutral and alkaline medium in contrast to the inactive Pt electrode. However, a pH dependence of the activity of nitrate reduction is observed on both Pt and Rh electrodes in acidic medium, in which medium the activity of nitrate reduction decreases as the solution pH increases. Relating the activity of nitrate reduction to the nitrate states (i.e. HNO_3 vs. NO_3^-) in solution as a function of pH, it is suggested that HNO_3 is the only reducible species for nitrate reduction on Pt, whereas both HNO_3 and NO_3^- are reducible species on the Rh electrode, so that a significant activity of nitrate reduction is sustained on Rh electrode above $\text{pH}=5$. Therefore, in acidic medium, it is better to speak of “nitric acid reduction” rather than “nitrate reduction”.

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Reference

- [1] M. Duca and M. T. M. Koper, *Energy & Environmental Science*, 2012, **5**, 9726.
- [2] V. Rosca, M. Duca, M. T. de Groot, and M. T. M. Koper, *Chemical Reviews*, 2009, **109**, 2209.
- [3] S. Taguchi and J. M. Feliu, *Electrochimica Acta*, 2007, **52**, 6023.
- [4] G. E. Dima, G. L. Beltramo, and M. T. M. Koper, *Electrochimica Acta*, 2005, **50**, 4318.

- [5] G. E. Dima, A. C. A. de Voors, and M. T. M. Koper, *Journal of Electroanalytical Chemistry*, 2003, **554**, 15.
- [6] M. T. de Groot and M. T. M. Koper, *Journal of Electroanalytical Chemistry*, 2004, **562**, 81.
- [7] J. F. E. Gootzen, P. Peeters, J. M. B. Dukers, L. Lefferts, W. Visscher, and J. A. R. van Veen, *Journal of Electroanalytical Chemistry*, 1997, **434**, 171.
- [8] S. Taguchi and J. M. Feliu, *Electrochimica Acta*, 2007, **52**, 6023.
- [9] S. Piao, Y. Kayama, Y. Nakano, K. Nakata, Y. Yoshinaga, and K. Shimazu, *Journal of Electroanalytical Chemistry*, 2009, **629**, 110.
- [10] M. C. Figueiredo, J. Souza-Garcia, V. Climent, and J. M. Feliu, *Electrochemistry Communications*, 2009, **11**, 1760.
- [11] E. B. Molodkina, M. R. Ehrenburg, Y. M. Polukarov, A. I. Danilov, J. Souza-Garcia, and J. M. Feliu, *Electrochimica Acta*, 2010, **56**, 154.
- [12] J. Yang, M. Duca, K. J. P. Schouten, and M. T. M. Koper, *Journal of Electroanalytical Chemistry*, 2011, **662**, 87.
- [13] M. C. Figueiredo, J. Solla-Gullón, F. J. Vidal-Iglesias, V. Climent, and J. M. Feliu, *Catalysis Today*, 2013, **202**, 2.
- [14] J. Souza-Garcia, E. A. Ticianelli, V. Climent, and J. M. Feliu, *Electrochimica Acta*, 2009, **54**, 2094.
- [15] M. Duca, M. O. Cucarella, P. Rodriguez, and M. T. M. Koper, *Journal of the American Chemical Society*, 2010, **132**, 18042.
- [16] M. Duca, M. C. Figueiredo, V. Climent, P. Rodriguez, J. M. Feliu, and M. T. M. Koper, *Journal of the American Chemical Society*, 2011, **133**, 10928.
- [17] O. Brylev, M. Sarrazin, L. Roué, and D. Bélanger, *Electrochimica Acta*, 2007, **52**, 6237.
- [18] M. da Cunha, J. P. I. De Souza, and F. C. Nart, *Langmuir*, 2000, **16**, 771.
- [19] P. Rodriguez, F. D. Tichelaar, M. T. M. Koper, and A. I. Yanson, *Journal of the American Chemical Society*, 2011, **133**, 17626.
- [20] O. Brylev, M. Sarrazin, D. Bélanger, and L. Roué, *Applied Catalysis B: Environmental*, 2006, **64**, 243.
- [21] S. C. S. Lai and M. T. M. Koper, *Faraday Discussions*, 2008, **140**, 399.
- [22] C. K. Rhee, M. Wasberg, P. Zelenay, and A. Wieckowski, *Catalysis Letters*, 1991, **10**, 149.
- [23] M. T. M. Koper, *Electrochimica Acta*, 2011, **56**, 10645.
- [24] R. Gisbert, G. García, and M. T. M. Koper, *Electrochimica Acta*, 2010, **55**, 7961.
- [25] M. J. T. C. van der Niet, N. Garcia-Araez, J. Hernández, J. M. Feliu, and M. T. M. Koper, *Catalysis Today*, 2013, **202**, 105.
- [26] O. Redlich, R. W. Duerst, and A. Merbach, *Journal of Chemical Physics*, 1968, **49**, 2986.
- [27] M. T. M. Koper, *Chemical Science*, 2013, **4**, 2710.
- [28] J. Joo, T. Uchida, A. Cuesta, M. T. M. Koper, and M. Osawa, *Journal of the American Chemical Society*, 2013, **135**, 9991.