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ARTICLE TYPE

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

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From a study of the electrocatalytic reduction of nitrate on Pt and Rh electrodes over a wide pH range, HNO_3 is suggested as the only reducible species in nitrate reduction on Pt, whereas both HNO_3 and the nitrate anion are reducible on Rh. Rh is the more active catalyst of the two because it can activate nitrate even if no protons are available in solution. This is an important insight for the development of more effective nitrate reduction catalysts.

Considerable attention has been paid to the electrochemical reduction of nitrate because of the necessity to convert nitrate in wastewater to dinitrogen, which is environmentally benign,[1] and also the opportunity to generate valuable products in the chemical industry, such as hydroxylamine and nitric oxide.[2]

Intense research 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 major focus of mechanistic studies of nitrate reduction, which has been shown to depend on nitrate concentration, electrolyte acidity and electrolyte anions,[2-7] and ammonia is the main (only) product of nitrate reduction in acid solution.[3, 5, 6] However, nitrate reduction on Pt electrodes is quite slow, and the Pt surface can be modified with another metal to enhance the activity of nitrate reduction and also lead to a specific formation of a certain product.[8-11] Even though nitrate reduction has been investigated mostly in acid media, 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 medium[12] and on Pd-modified Pt(100) in alkaline medium,[13] 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 N_2 as products.[14, 15]

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In contrast, rhodium shows higher activity and a weaker influence of anions in acid than platinum,[5] and ammonia was found as the main product.[16, 17] Moreover, if Rh is alloyed with a low amount of Pt ($Rh_{80}Pt_{20}$), a higher nitrate reduction activity was found compared to pure Rh in sulfuric 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; ammonia formation dominates in acid medium whereas nitrite formation dominates when the solution pH is above 7.[16, 19] 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, in this communication, we investigated nitrate reduction in a wider pH range on both Pt and Rh electrodes, and based on these results we will be able to formulate a new model for the pH dependent reactivity of nitrate, which is of general importance to developing new nitrate reduction catalysts.

The cyclic voltammograms of a polycrystalline Rh electrode were recorded in phosphate solution over a broad pH range until a stable shape was obtained at the scan rate of 50 mV/s (see Figure S1, ESI). They 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.[20] 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 S1(b) shows that a linear relationship exists between the peak potentials (on the RHE scale) and solution pH. 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.[21] 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,[22] 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.[22] Thus, we assume that the same holds for Rh, though this would really necessitate measurements in a solution free of strongly adsorbing anions.
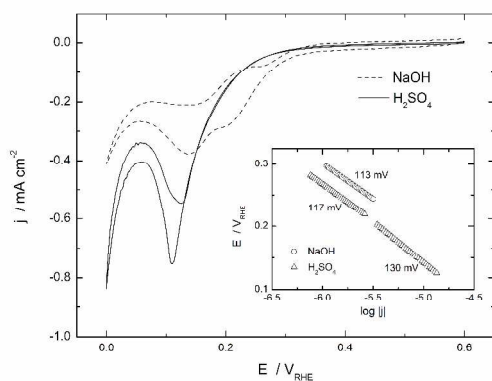

Figure 1 A comparison of nitrate reduction on a Rh polycrystalline electrode in 0.1 M H_2SO_4 and 0.1 M NaOH solution with 10 mM $NaNO_3$ at the scan rate of 5 mV/s. The inset shows the Tafel plot obtained from the voltammetry at 1 mV/s in the negative-going scan.
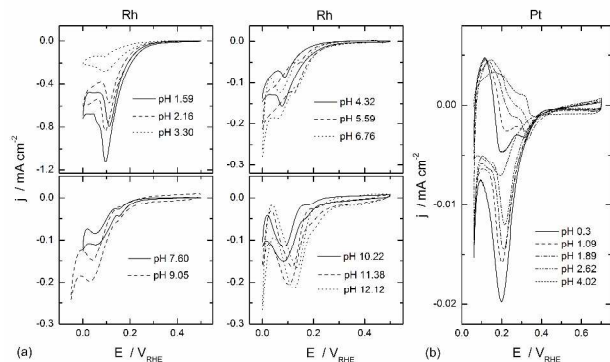

Figure 2 Cyclic voltammograms of nitrate reduction on (a) Rh polycrystalline electrode in a wide pH range of phosphate buffer solution and (b) Pt polycrystalline electrode in acidic perchlorate solution, at the scan rate of 5 mV/s.

The voltammetry of nitrate reduction in 0.1 M H_2SO_4 and 0.1 M NaOH solution is compared in Figure 1. 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 ~ 0.1 V. The peak is most likely due to 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 increases at approximately the same potential as in H_2SO_4 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. The surface adsorbed intermediate from nitrate reduction on Rh in acid was measured by potential stripping from a clean 0.1 M H_2SO_4 solution (see Figure S2). The cathodic peak at 0.22 V from the first scan corresponds to the NO_{ads} reduction on Rh surface,[23] with a charge of about 344 $\mu C/cm^2$, where the reduction of co-adsorbed oxygen-containing species probably also contributed to the reductive stripping charge.[24, 25] Tafel slopes were obtained from the onset on nitrate reduction, as shown in the inset in Figure 1. For both acid and alkaline media, similar slopes of ca. 113 mV dec^{-1} were found for potentials above 0.22 V. This indicates that the rate-determining step is independent of the solution pH.

The nitrate reduction was investigated on Rh and Pt over a wide pH range from 2 to 12 (see Figure 2). 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 3, 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 over the whole pH range investigated (see Figure 3(c)).
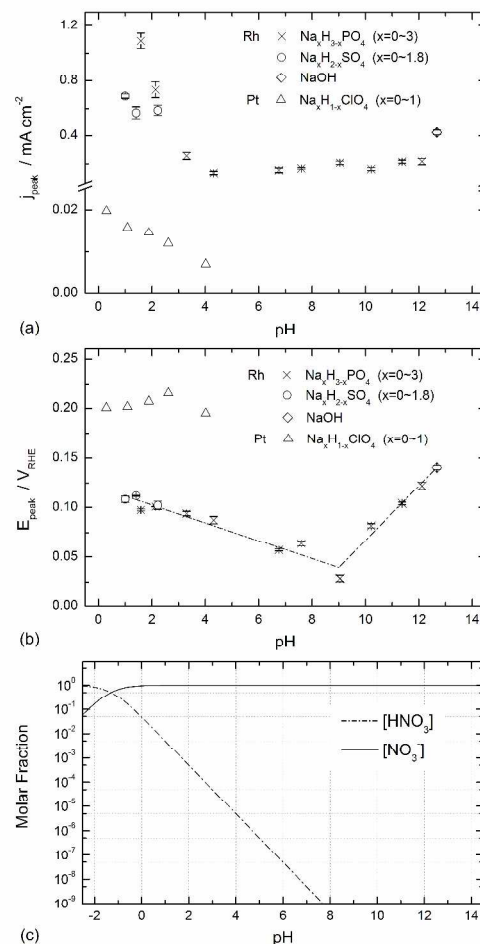

Figure 3 Variation of (a) peak current densities and (b) peak potentials for nitrate reduction on Pt and Rh electrodes over a wide pH range. The peak values were acquired from cyclic voltammetry at the scan rate of 5 mV/s. The experiments for Rh were repeated 3 times. (c) shows the molar fractions of 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 2(b) and 3(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 on Rh 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 3(b) shows how the voltammetric peak potential 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 is the same as in alkaline and 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:

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \qquad (1)$$
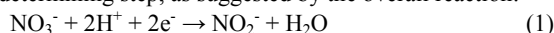
In solution there is equilibrium between nitrate and nitric acid, and their molar fractions as a function of the solution pH are shown in Figure 3(c). The concentration of nitric acid decreases exponentially as the solution pH increases and is practically negligible (i.e. < 1 μM) for pH>5, whereas the concentration of nitrate can be considered constant for all pH>0. Relating the trend in peak current densities on Pt and Rh electrodes to the concentrations of HNO_3 and NO_3^- in the same pH range, we suggest the following explanation for the pH dependence of nitrate reduction. On the Pt surface, the HNO_3 molecule is the only active species, whereas on the Rh surface both HNO_3 and NO_3^- are actively reducible species with HNO_3 being more reactive. 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 HNO_3 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 HNO_3, due to the ability of Rh to activate NO_3^-. However, the HNO_3 form is considered as a considerably more easily reducible species than NO_3^- on both Pt and Rh electrode surfaces (i.e., HNO_3 has a much higher rate constant for reduction than NO_3^-), and therefore a higher activity is observed in a solution of high 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. pH=-1.3, as this optimizes the reactivity of the most reactive species,[27, 28] but measurements at such high acidity are complicated, because the indirect mechanism of nitrate reduction, is dominant in acid media.[6] We note that the exact functional dependence of the current on pH requires a detailed kinetic model and detailed experiments in which the role of the concentration of supporting electrolyte can be ruled out. Figure 3a may appear to suggest a linear dependence but we stress that those experiments were not designed to obtain a clean functional dependence on pH.

Conclusions

Nitrate reduction has been investigated on Pt and Rh polycrystalline electrodes in a broad pH range. The Rh electrode is active in both neutral and alkaline medium in contrast to the Pt electrode. 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 degree of protonation of nitrate 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 pH=5. Therefore, in acidic medium, it is better to speak of "nitric acid reduction" rather than "nitrate reduction". Further evidence for this idea may come from in situ infrared spectroscopy, such as in the study by Nakata et al.[29] Still, the pH dependence displayed in this communication is convincing evidence for how catalytic proton-coupled electron transfer reactions may sensitively depend on pH due to acid-base equilibria in solution.[27, 28]

Acknowledgement

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