

Supporting information to

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

Jian Yang,^a Paula Sebastian,^a Matteo Duca,^{a, b} Thijs Hoogenboom^a and Marc T. M. Koper^{*a}

^a Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

^b Université Paris Diderot, Sorbonne Paris Cité, Laboratoire d'Electrochimie Moléculaire, Unité Mixte de Recherche Université–CNRS no. 7591, Bâtiment Lavoisier, 15 Rue Jean de Baïf, 75205 Paris Cedex 13, France.

* To whom all correspondence should be addressed. E-mail: m.koper@chem.leidenuniv.nl

Experimental

All experiments were carried out at room temperature and ultrapure water (Millipore MilliQ, resistivity > 18.2 MΩ cm) was used to prepare solution. The electrochemical cell and glassware used in the experiment were cleaned in acid according to a procedure described elsewhere¹ and then boiled with ultrapure water. NaNO₃ (Merck, 99.99%) was applied to study the nitrate reduction in different solutions. Phosphoric acid (Merck, suprapur), NaH₂PO₄ (Merck, 99.99%), Na₂HPO₄ (Merck, 99.99%) and Na₃PO₄ (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, suprapur) and NaClO₄ (Merck, suprapur) were used to prepare the perchlorate solution; sulfuric acid (Merck, suprapur) and Na₂SO₄ (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,² 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 H₂ (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).

Adsorbate on Rh electrode was obtained from nitrate reduction by keeping Rh electrode contact with nitrate solution under potential control for 200 s. And then Rh electrode was rinsed and transferred to the electrochemical cell containing 0.1 M H₂SO₄ solution. The electrode potential was kept at 0.55 V before the cyclic voltammetry measurement.

Results

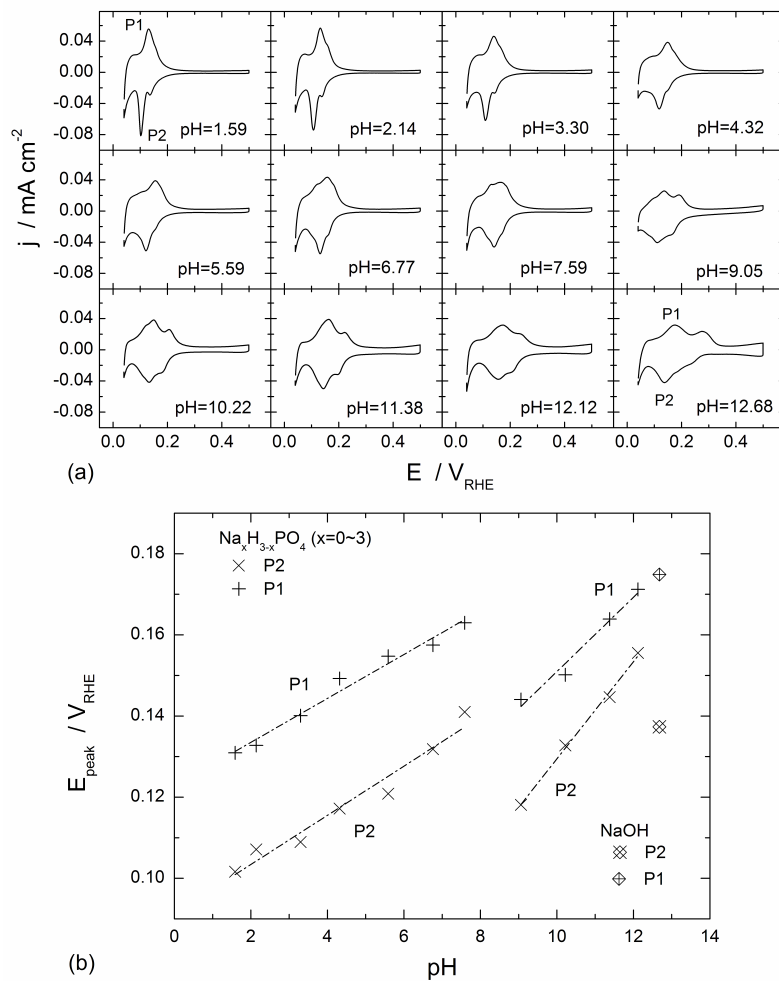


Figure S1 (a) The cyclic voltammograms of a polycrystalline Rh electrode in solutions of different pH at a scan rate of 10 mV/s and (b) the pH dependence of peak potentials of P1 and P2.

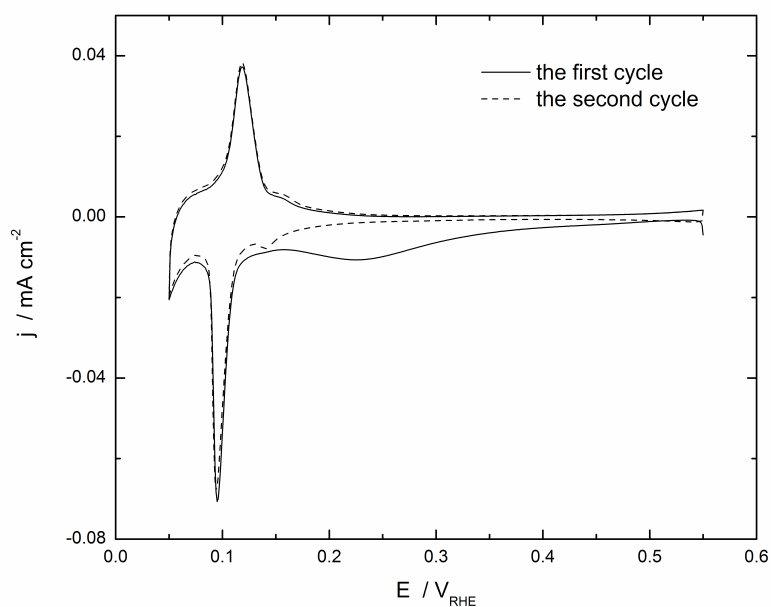


Figure S2 The voltammogram of adsorbate stripping on Rh electrode in 0.1 M H₂SO₄ solution at a scan rate of 5 mV/s. The adsorbate on Rh electrode was obtained under potential E = 0.25V.

Reference

1. S. C. S. Lai and M. T. M. Koper, *Faraday Discuss.* 2008, **140**, 399-416.
2. C. K. Rhee, M. Wasberg, P. Zelenay and A. Wieckowski, *Catal. Lett.* 1991, **10**, 149-164.