

The Electrochemistry and Electrochemical Technology of Nitrate

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I. INTRODUCTION

The cathodic reduction of nitrate is a truly fascinating reaction. It can lead to at least eight different products in reactions involving the transfer of one to eight electrons per nitrate ion, see Fig. 1. A mixture of products is usual and it is never obvious whether products are being formed in a sequence of electron transfer steps or by parallel reduction mechanisms. Two consequences follow. Firstly, simply the determination of the average number of electrons involved in the reduction is a very poor indicator of the likely products. Secondly, it is apparent that the product spectrum is likely to depend on a number of experimental parameters including the concentration of nitrate and pH as well as cathode material, electrode potential (or current density) and charge passed. All the reduction reactions of nitrate involve protonation and hence the local pH at the cathode surface can be quite different from the bulk value and it can vary during an experiment, e.g. during a potential sweep. Particularly with high nitrate concentrations, (and/or high current density), the reaction layer will only be buffered in

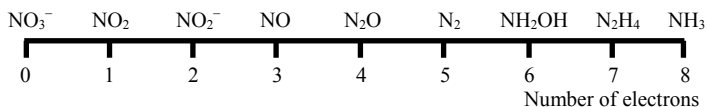


Figure 1. Possible products from the reduction of nitrate ion.

solutions at the extremes of pH; buffers added to the solution of nitrate have a strong influence on the reduction of nitrate, even killing the response entirely. Moreover, experience shows that the presence of both cations and anions (including nitrite) at a trace or impurity level can lead to changes in the product spectrum; hence, the purity of chemicals and water used in the preparation of solutions is an issue in all experimental studies. Certainly, product selectivity is a concern in all applications involving the reduction of nitrate ion. Also, hydrogen evolution is usually a competing reaction producing multiple challenges for electrocatalysts—enhancing the rate and selectivity of nitrate reduction while minimising hydrogen evolution. In addition, perhaps not surprisingly, the mechanisms for nitrate reduction remain very poorly understood; most perplexing, the mechanisms are least understood when the voltammetry is simplest!

Despite these difficulties, there are several reasons why nitrate reduction is of interest to electrochemical technology. Processes have been developed for the removal of nitrate from both, drinking water and effluents, for the reduction of nitrate as an essential step in nuclear waste disposal and for the manufacture of hydroxylamine while both electroanalytical procedures and sensors for nitrate have been described. Some of these objectives have also been approached by electrochemical membrane technology using approaches not involving the cathodic reduction of nitrate and the final section of this chapter will also review such methods.

We are not aware of any extensive reviews of the electrochemistry of nitrate since the chapter by Plieth published in 1978.¹

II. THERMODYNAMICS OF NITRATE REDUCTION

As noted above, a number of products (namely nitrite ion, oxides of nitrogen, nitrogen, hydroxylamine, hydrazine and ammonia)