

## Discovery of Cathodic Nitrogen Evolution

Sharon G. Roscoe and Brian E. Conway\*

*Chemistry Department, University of Ottawa, 32 George Glinski Way, Ottawa, Ontario K1N 6N5, Canada*

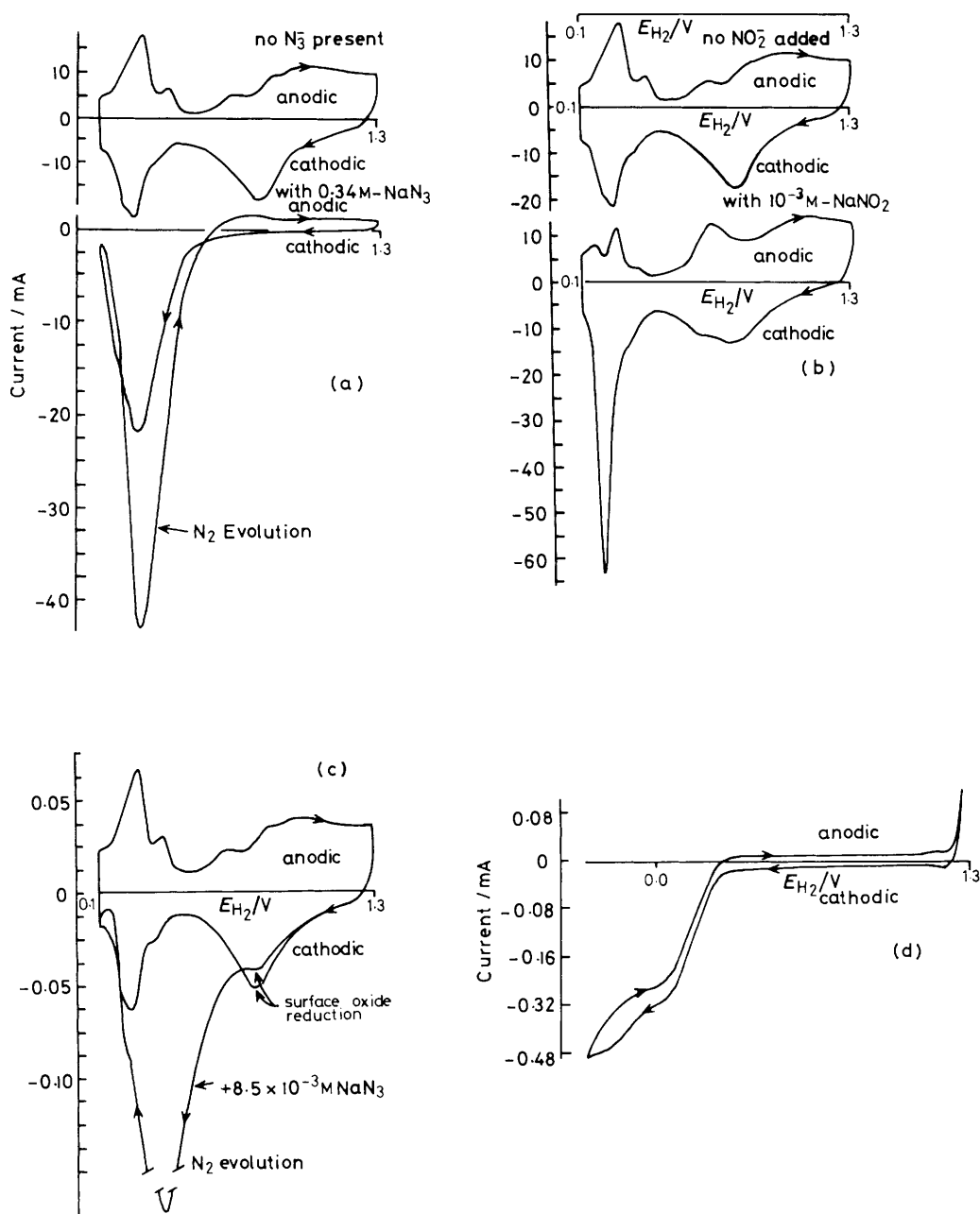
During cyclic voltammetry studies of the surface electrochemistry of the oxidation of azide ions to  $N_2$  at a Pt anode, a large reduction current peak is observed during the cathodic sweep; this is shown to be due to electrolytic reduction of  $N_3^-$  to  $N_2$  gas and aqueous  $NH_3$ .

A new electrochemical gas reaction, the cathodic evolution of  $N_2$  from azide ion in aqueous solution, has been discovered during the course of surface electrochemistry investigations on the known anodic nitrogen evolution reaction.<sup>1-3</sup> Decomposition of  $N_3^-$  by discharge at an anode, according to the overall reaction  $2N_3^- \rightarrow 3N_2 + 2e$ , is not unexpected, although the mechanism, which presumably<sup>1-3</sup> involves initial formation of  $N_3^*$ , is not well established. As with some other anodic processes, in aqueous solution at noble metals,  $N_3^-$  discharge takes place on a surface oxide film generated at potentials below those for discharge of the anion.

During a study<sup>4</sup> of the state of Pt anodes at which anodic  $N_2$  evolution was occurring from the electrochemical decomposition of  $N_3^-$  at *ca.* +1.7 V (relative to the hydrogen electrode), cyclic voltammetry experiments were employed to determine,

in the reduction sweep, the state and extent of formation of the surface oxide film formed prior to and during anodic  $N_2$  evolution, as was done analogously in our studies of anodic  $Cl_2$  evolution at Pt.<sup>5</sup> In the cathodic sweeps of the cyclic voltammograms at Pt in  $N_3^-$  solution, a large reduction current peak, associated with visible gas evolution, arose at +0.30 V [Figure 1(a)], overlapping the current profile for reduction of the Pt oxide film formed on the previous anodic sweep. In fact, the Pt oxide reduction current, determined in the presence of  $N_3^-$ , was much diminished owing to competitive adsorption between  $N_3^-$  and OH and O species, as with  $Cl^-$  adsorption.<sup>5</sup>

Potentiostatic electrolysis at 0.3 V gives continuous gas evolution, cathodically, but at a rate diminishing with time; reactivation to a high rate arises, however, when the potential



**Figure 1.** Cyclic voltammograms at 298 K for: (a) a Pt electrode in 0.34 M NaN<sub>3</sub>, showing large reduction current at ca. 0.30 V; (b) a Pt electrode in 0.1 M NaOH + 0.001 M NaNO<sub>2</sub> in the absence of N<sub>3</sub><sup>-</sup>; (c) a Pt electrode in 0.1 M NaOH + 8.5 × 10<sup>-3</sup> M NaN<sub>3</sub> showing the distinction between the Pt surface oxide reduction peak and the azide-dependent reduction peak at less positive potentials; and (d) an Au electrode in aq. 1 M NaN<sub>3</sub>.

is pulsed again to give anodic N<sub>2</sub> evolution (*i.e.* with reoxidation of the Pt surface), and then returned to 0.3 V. Thus, the cathodic process is self-inhibited at the potential at which it takes place spontaneously. This is consistent with the observation that the cathodic current at controlled potential is diminished by rotation at a Pt disc electrode, which implies a negative order in [N<sub>3</sub><sup>-</sup>] for the reaction, as confirmed by direct rate measurements over a range of N<sub>3</sub><sup>-</sup> concentrations.

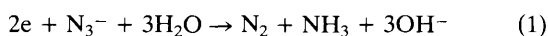
Since the cathodic current peak is increased after polarization to the anodic N<sub>2</sub> evolution potential but decreased by electrode rotation after such a procedure, it is possible that NO<sub>2</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup> ions are formed in the anodic potential sweeps; either or both of these species could give rise to the

reduction current peak in the following cathodic sweeps. An experiment in which NaNO<sub>2</sub> was added in small quantity to 0.1 M NaOH in the absence of N<sub>3</sub><sup>-</sup> did in fact give a reduction current peak [Figure 1(b)], but its potential (+0.20 V) was less positive than that of the peak observed in the presence of N<sub>3</sub><sup>-</sup>; also the peak was observed only in the cathodic sweep and not in the return anodic sweep, whereas with N<sub>3</sub><sup>-</sup> the peak was observed [Figure 1(a)] both in the cathodic and in the subsequent anodic sweep (prior to Pt surface oxidation). Hence the reduction current is not due to incidental formation of NO<sub>2</sub><sup>-</sup>. No reduction current was found after addition of NO<sub>3</sub><sup>-</sup> ion.

Since the cathodic current peak arises at a potential more

positive than that for cathodic deposition of H<sub>2</sub> or for underpotential deposition of H at Pt, but much less positive than for anodic N<sub>2</sub> or O<sub>2</sub> evolution, the cathodic current must arise from reduction of N<sub>3</sub><sup>-</sup> to gaseous N<sub>2</sub>. The continuous nature of this current and its distinction from the non-continuous current profile for Pt surface oxide reduction [Figure 1(c)] preclude its assignment to the latter process.

If aqueous N<sub>3</sub><sup>-</sup> undergoes a two-electron reduction to N<sub>2</sub>, elementary chemical considerations require that NH<sub>3</sub> must also be a product [equation (1)]. Although the reductive formation of N<sub>2</sub> from N<sub>3</sub><sup>-</sup> is most probably irreversible, it is of interest to calculate from thermodynamic data<sup>6</sup> the potential for reaction (1): it is +0.20 V (relative to the hydrogen electrode) at 298 K, if we take into account the measured concentration of NH<sub>3</sub> in solution (see later). The observed potentials of the current peak at Pt are +0.30 and 0.20 V, in the cathodic and anodic directions of sweep, respectively, in surprising agreement with the thermodynamic value.



In order to confirm that the observed process is reaction (1), potentiostatic gas and solution analysis experiments were carried out in a gas-tight cell of small volume, outgassed and filled with He. Small quantities of the evolved gas were collected and analysed in a directly attached gas chromatograph. The evolved gas was identified as mainly N<sub>2</sub> together with a small quantity of O<sub>2</sub>, probably arising from the anodic pulse activation procedure required to maintain the electrode in an active condition for cathodic N<sub>2</sub> evolution. The cell and analysis system gave a zero N<sub>2</sub> + O<sub>2</sub> 'air blank' when He was bubbled in the absence of azide electrolysis. Dissolved NH<sub>3</sub>

was also identified by means of Nessler's reagent after controlled extents of electrolysis, and the quantities generated were related to the yields of N<sub>2</sub> and to the coulombic charges passed.

Thus the occurrence of reaction (1) is confirmed: cathodic evolution of N<sub>2</sub> occurs in the reduction of azide ion. Final confirmation was provided by observation of the reduction current peak, with visible gas evolution (N<sub>2</sub>) immediately on the first cathodic sweep at *ca.* +0.3 V after NaN<sub>3</sub> was added to aq. 0.1 M NaOH already undergoing cyclic voltammetry.

Comparable experiments at Au also give rise to cathodic N<sub>2</sub> evolution from N<sub>3</sub><sup>-</sup> but the N<sub>2</sub> current increases until it overlaps with the increasing H<sub>2</sub> current [Figure 1(d)], *i.e.* without passing through the maximum observed at Pt [Figure 1(a)]. This difference is probably due to inhibition of N<sub>3</sub><sup>-</sup> adsorption at Pt due to underpotential deposition of H which is not significant at Au.

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