

The Nitric Acid-Air Redox Electrode

Joseph A. Shropshire and Barry L. Tarmy

Process Research Division
Esso Research and Engineering Company
Linden, New Jersey

One approach to the development of a satisfactory oxygen or air electrode for a fuel cell operating in an acid electrolyte is the use of a so-called redox electrode. Such a system utilizes the more favorable electrochemical activity of a secondary oxidant with the electrochemical reduction products regenerated chemically by oxygen or air. In this manner it is possible to obtain higher electrical performance than is attainable by direct electrochemical reduction of oxygen. This increased performance is of particular significance in the operation of air electrodes, where high concentrations of nitrogen seriously affect electrode efficiency. Recent reports have cited the use of $\text{Br}^- - \text{Br}_2$ and $\text{Ce}^{+4} - \text{Ce}^{+3}$ for this purpose (1,2). However, these systems have shown serious limitations in practical operation.

This paper describes the performance and mechanism of operation of another redox cathode, one based on the reduction of nitric acid in sulfuric acid. Previous investigators have studied the cathode reaction on platinum in $\text{HNO}_3/\text{HNO}_2$ systems under various conditions (3,4,5,6). However, none of these considered the possibility of using this system as a redox oxygen electrode. Furthermore, with the acid concentrations used, the presence of HNO_3 could seriously impair the performance of a fuel electrode. With the intent of avoiding this difficulty, a study has been made of the redox behavior of low concentrations of HNO_3 in sulfuric acid electrolyte. The results of that study are presented here.

EXPERIMENTAL

All electrochemical measurements described here were carried out in conventional glass cells with either parallel or coaxial electrode arrangements. Anode and cathode compartments were separated by either glass frits or cationic exchange membranes. Noble metal and carbon electrodes were employed and performance in most cases was obtained during operation against a "driven" counterelectrode, power being supplied by 6-12 volt regulated D.C. sources. All solutions were prepared using C.P. grade sulfuric (96.5%) and nitric (70%) acids diluted with deionized water of conductivity 10^{-6} mho/cm. Electrode voltages were measured against commercial saturated calomel electrodes equipped with Luggin capillary probes. Voltages and current measurements were obtained with Keithley electrometers of 10^{14} ohms input impedance.

More specific details, when necessary, will be found in the text. All electrode potentials reported herein are referred to the standard hydrogen electrode (N.H.E.), and sign conventions conform to the adopted standards. No attempt has been made to correct the voltage measurements for liquid junction and thermal potentials, the magnitude of which may be significant in strong acids, about 50 to 100 mv.

PERFORMANCE OF THE HNO₃ REDOX ELECTRODE

The initial performance tests using platinized-carbon oxygen electrodes in 3.7 M H₂SO₄ at 80-82°C., indicated that the addition of 0.2 M HNO₃ to the H₂SO₄ electrolyte resulted in large improvements in performance as measured by conventional voltage-log current plots. Further tests indicated that these improvements were not limited to carbon based electrodes alone, but were also attainable with noble metal electrodes. The performance, an example of which is shown in Figure 1, was found to be independent of the supply of primary oxidant, i.e., oxygen or air, but did depend on both HNO₃ and H₂SO₄ concentrations.

Typical E-log I plots showed little evidence of a well defined Tafel slope. At temperatures above 50°C. open circuit potentials as high as 0.92 volts vs the calomel reference were obtained. Neglecting liquid junction and thermal potentials, this is equivalent to 1.16 volts vs N.H.E. High performance in a fresh electrolyte was shown to occur only at temperatures in excess of 50°C., but accumulation of reduction products with continued operation enabled the return of the system to 25°C. with retention of relatively high performance levels.

Furthermore, coulometric determinations in the experiments with oxygen showed that the number of coulombs involved was far greater than that needed to account for reduction of all HNO₃ in the system. Thus a redox cycle exists, consisting of an electrochemical reduction of some species in the HNO₃ system and the reoxidation of the products by oxygen.

Concentration Variables

A concentration variable study was carried out in which performance (E vs log I) and limiting currents were determined for a series of electrolyte compositions covering the range of 0.2- 1.0 M HNO₃ at a H₂SO₄ concentration of 3.7 M, and 0.5-3.7 M H₂SO₄ at a HNO₃ concentration of 0.2 M. The results of this study showed that limiting currents were not only linearly dependent on HNO₃ concentration (Figure 2), but were also linearly dependent on the proton activity in the system neglecting the contribution from the HNO₃ (Figure 3). It was also observed that for these systems limiting currents decreased with increasing agitation of the electrolyte. The data, therefore, are reported with respect to a fixed rate of gas flow agitation or at quiescent conditions. Similar observations of decreasing limiting currents with increasing agitation were made by previous investigators in HNO₃/HNO₂ systems (4,6).

Effects Of Temperature

Variation of the HNO₃ electrode activity with temperature was studied in the range of 50-106°C. Limiting currents were measured with the electrolyte solution presaturated with either O₂, N₂ or NO. The data provided a straight-line plot of log limiting current vs reciprocal absolute temperature (Figure 4) with a slope corresponding to an activation energy of about 10 kcal/mol for all three gases. An activation energy of this magnitude indicates a chemical rate-limited rather than diffusion limited current. The absolute level of the limiting currents varied, however, among the three gases used. This effect will be discussed in a later section.

MECHANISM STUDIES

These data suggest a relatively complex reaction mechanism. Furthermore, it was felt that the practical development of this redox system for fuel cell use would require a complete knowledge of the reduction and regeneration reactions. Consequently, studies were directed toward establishing the reduction mechanism and determining the reaction products.

Cathodic Transients

A system was assembled to investigate the response of an electrode to constant current pulses during the HNO_3 reduction reaction. Current pulses were applied to the electrode in a 3.7 M H_2SO_4 —0.2 M HNO_3 electrolyte at 82°C. Constancy of current (< 1%) was obtained using a high voltage (175 V.) D.C. regulated power supply and a high series resistance. Voltage transients, measured against a saturated calomel electrode-Luggin capillary arrangement, were displayed on a Tektronix 545A oscilloscope (Type D—D.C. Preamp.) and photographed. Input impedance of this oscilloscope (10^6 ohms) represented an insignificant load in the voltage measuring circuit.

Voltage-time variations at constant current can be analyzed in terms of the transition time, τ . This transition time is a function of concentrations, diffusion coefficients and current density for reactions under diffusion control (7). It is measured from the inception of the reaction wave to its inflection (see Figure 8) and can be used analytically as a measure of concentration of a reacting species. Thus,

$$i \tau^{\frac{1}{2}} = \frac{\pi^{\frac{1}{2}} n F C^{\circ} D^{\frac{1}{2}}}{2}$$

where C° is the bulk concentration of the reacting species and all other symbols have their usual significance.

Initial experiments with this technique confirmed that HNO_3 itself was not directly reduced. Under conditions where diffusion controlled transition times for HNO_3 reduction would be expected to begin at about +0.95 volts vs N.H.E. and to exceed 10 seconds duration, observed transition times at this level were less than 0.1 second. Transients at currents slightly less than that required for complete polarization showed autocatalytic behavior. Typically the electrode polarized several tenths of a volt and rapidly recovered to more positive voltages all at constant current load. (Figure 5) The reaction wave at more negative potentials in Figure 5-A disappeared upon degassing with N_2 .

The extreme autocatalytic nature of the electrode reaction was further emphasized by transients observed following extended periods of cathodization and under conditions of repetitive current pulses. An electrode placed in a fresh electrolyte solution extensively sparged with O_2 polarized completely to H_2 evolution potentials upon application of a 1 ma/cm² current pulse. Upon slowly increasing the current from zero, however, a level of 5 ma/cm² was easily obtained. After five minutes cathodization at this level followed by several seconds at open circuit, the electrode withstood a current pulse of 66 ma/cm² with equilibrium polarization of only 0.1 volts (Figure 6). A gradually improving response could be observed with repetitive current pulses in a fresh solution as shown in Figure 7.

Based on the high temperature dependence of the limiting currents, and absence of a well defined tafel slope, a reduction reaction with chemical rate-limitation is indicated. The dependence of limiting currents on HNO_3 concentration, in conjunction with the autocatalytic behavior, suggests that this rate limiting step involves reaction of a product species with the HNO_3 itself to produce the electrochemical reactant.

Product Identification

To clarify the mechanism and assess the possibilities of this system as an efficient redox electrode, experiments were run to establish the identity of the reaction products. A cell with 3.7 M H_2SO_4 - 0.2 M HNO_3 electrolyte containing a

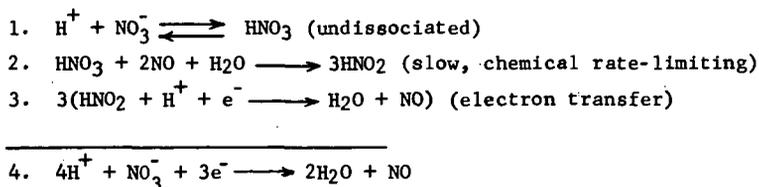
large auxiliary cathode was used for reacting the nitric acid. Another electrode (0.27 cm² in area) was placed in close proximity and used as a product detection device. At desired intervals this electrode was supplied with an anodic current pulse to reoxidize the product material present. The potential transient produced was recorded photographically from the oscilloscope trace. A typical transient found for product reoxidation is shown in Figure 8. Using this technique, it was possible to follow the build-up of product and its rate of disappearance under conditions of O₂ or N₂ sparging. It was found that the product was removed during both N₂ and O₂ sparging but that removal occurred more rapidly with O₂ sparge, suggesting reaction with O₂. The data obtained are shown in Figure 9, where $1/i \cdot \tau^{1/2}$ is recorded versus sparge time. This quantity, as previously described, is proportional to reciprocal concentration ($1/C_R$) of the reacting species.

This evidence strongly indicated NO as the electrochemical reaction product. This conclusion was confirmed by observations on transients obtained in an air-free 3.7 M H₂SO₄ solution saturated with NO gas. Transients obtained in this system were identical to those of Figure 8. Furthermore, saturation of the H₂SO₄-HNO₃ electrolyte with NO caused the complete absence of all autocatalytic effects previously observed.

The effect of temperature on limiting current in this latter system was previously shown in Figure 4. The increase in limiting currents in this NO equilibrated solution over those obtained with O₂ and N₂ also affirms the role of NO as the electrochemical product which participates in the chemical rate limiting step. Limiting currents with NO are not disproportionately high, however, since electrochemical NO evolution at the limiting current is sufficient to essentially saturate the solution in the vicinity of the electrode.

Proposed Mechanism

Based on the observed behavior, the over-all mechanism of the cathodic reaction in the 3.7 M H₂SO₄ - 0.2 HNO₃ electrolyte would seem best suited by the following scheme:



As previously indicated, the rate limiting step is the slow chemical production of HNO₂, the electrochemical reactant. Reaction 3 is assumed to operate reasonably reversibly, with the potential at any given current density being fixed by the local ratio of HNO₂ and NO activities. At the limit of the chemical reaction rate, the concentration of HNO₂ at the electrode surface falls to zero and the potential increases until another reaction potential is reached. This scheme takes full account of the observed dependence of limiting current on stirring, since excess agitation tends to remove the product NO, making it unavailable for reaction 2 near the surface. The dependence of limiting current on both HNO₃ and H₂SO₄ concentration probably indicate that HNO₃ is undissociated in reaction 2.

Minc (3) has studied polarization curves for platinum electrodes in HNO_3 . He found that the high positive potential cathode process takes place only in solutions of HNO_3 at concentrations sufficient to contain appreciable amounts of the nonionized form of nitric acid. His work indicates a linear relation between the log of the concentration of the nonionized form and electrode voltage at constant current values in the Tafel region. In our high proton activity solutions, it is expected that significant quantities of nonionized HNO_3 also exist. Thus, equilibrium of reaction 2 at low current densities would result in a similar dependence on acid concentration.

The mechanism proposed here differs from the one advanced by Vetter (6) to account for similar effects in the system $\text{HNO}_3/\text{HNO}_2$ at 25°C . That investigator, following the earlier work of Beinert et al. (8), measured anodic and cathodic polarization curves in various $\text{HNO}_3/\text{HNO}_2$ systems. He concluded that the reduced species of the reactive electrochemical couple was HNO_2 or a species in rapid equilibrium with HNO_2 (e.g., NO , NO_2^- , etc.). Vetter derived a mechanism involving the reduction of NO_2 to HNO_2 and entrance of the product HNO_2 into a rate limiting chemical step analogous to reaction (2). The distinction between these mechanisms rests on two observations:

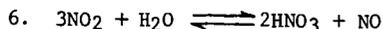
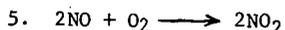
(1) Since there is little likelihood of further reduction beyond NO (the observed product) the reaction wave in Figure 5-A which is removed by degassing must represent NO_2 reduction. This is reinforced by the fact that spontaneous reversion to the low polarization level of activity ($\sim + 0.97$ volt vs N.H.E.) occurs upon reaching this reaction plateau. Such behavior would occur if this reaction level represented another source of HNO_2 , i.e., by a one-electron electrochemical reduction of NO_2 . Thus, if insufficient HNO_2 is available to support the reaction at the low polarization level, the system has a built-in "safety" for electrochemical HNO_2 production at the higher polarization, if sufficient NO_2 is present in solution.

(2) As was indicated earlier, saturation of degassed 30% H_2SO_4 with NO gas alone produced an anodic transient identical to that observed for the product of the cathodic reaction. Moreover, this oxidation wave of NO , and the observed cathodic reaction wave are symmetrical about the observed rest potential of the system. It would then appear that NO , rather than HNO_2 , is the reduced component of the reversible couple operating at this potential. The reduction wave in Figure 5-A, presumed to be NO_2 , occurs at much less positive potentials.

Vetter's work was carried out at 25°C . and in general much higher HNO_3 concentrations than were employed in this study. Thus there need be no direct relationship between the behavior observed in these systems. At low nitric acid concentrations Ellingham (5) points out the importance of reaction 2 in determining the equilibrium between NO and HNO_3 .

REGENERATION

With no regard to the mechanism involved, it has been definitely established that the net product of the cathode reaction is gaseous NO . Thus the problem of completing the redox cycle by conversion of NO to HNO_3 then becomes a process well known in the nitric acid production industry (9). The reaction goes by the scheme:



Reaction 5 is a classical termolecular reaction with negative energy of activation, favored by low temperature and high pressure. Reaction 6 at normal pressures is not limiting but suffers the drawback that NO is produced, thus requiring infinite reaction space for completion of reactions 5 and 6. On a practical basis, however, sufficient NO conversion is obtained by maximizing gas contact times before and during hydrolysis.

Using standard methods of contacting the NO produced at the electrode with O₂ and the electrolyte, it is possible to regenerate HNO₃ to the extent that the electrochemical cathode process of HNO₃ reduction may be carried out for periods of time equal to several times the coulombic equivalent of HNO₃ added. However, under carefully optimized O₂ regeneration conditions, it has been possible in our laboratories to pass currents at low polarization equal to 225 times the coulombic equivalent of the HNO₃ lost from the system. Under comparable conditions, this number with air is about 30. Operation at this regeneration efficiency reduces the amount of HNO₃ make-up to a small quantity, about 0.1 lb/kwh.

COMPATIBILITY

Although it is not the purpose of this paper to deal with the operation of entire fuel cell systems, a few words concerning compatibility seem appropriate. Due to the highly active oxidizing nature of the cathode reactant, it is necessary to carry out the cathode reaction at the lowest possible nitric acid concentration consistent with the current required. A nitric acid concentration of 0.2 M is sufficient to obtain currents of 75-100 ma/cm².

The effect of HNO₃ on the opposing electrode generally will be less with highly electroactive anode fuels. Thus, a fuel such as H₂ will suffer least. Deleterious effects seem to arise primarily from accumulation of intermediate species in the HNO₃ systems, e.g. HNO₂, NO₂, and thus efficient regeneration on the cathode side increases compatibility. For instance, addition of HNO₃ at concentrations below 0.6 M directly to a separated anolyte compartment causes no deleterious effects at an operating methanol electrode. Effects were evident, however, at 0.25 M when an operating HNO₃ cathode was not separated from the anode compartment and reduction products were allowed to accumulate.

SUMMARY

The use of HNO₃ in a fuel cell cathode redox cycle has been shown to provide improved cathode performance over that generally achieved with direct electrochemical reduction of O₂. The system provides equal electrical performance using either O₂ or air. The product of cathode reaction in this system is gaseous NO and efficiency of the redox cycle depends on its reconversion to HNO₃. While both oxygen and air provide high levels of regeneration, oxygen, as would be expected, shows superiority. A consistent mechanism has been advanced to account for all aspects of the cathode reaction in this system. Basic rate limitation in the electrochemical reduction reaction appears to be a chemical step involving the reaction of NO and HNO₃.

The redox concept, as applied here, can of course be extended in principle to improvement of any electrode reaction where reactants exhibit low electroactivity. The requirements naturally necessitate that the redox intermediate be less easily reduced (or more difficultly oxidized) in theory than the oxidant (or fuel) species to be replaced. Thus while actually exhibiting more electrochemical activity than the oxidant or fuel to be replaced, the chemical regeneration of the intermediate is still feasible. For most practical fuel cell systems, the redox intermediate would thus be restricted to those couples exhibiting reversible potentials not more than about 0.2 volts less positive (or 0.2 volts more positive) than the oxidants (or fuels) to be replaced.

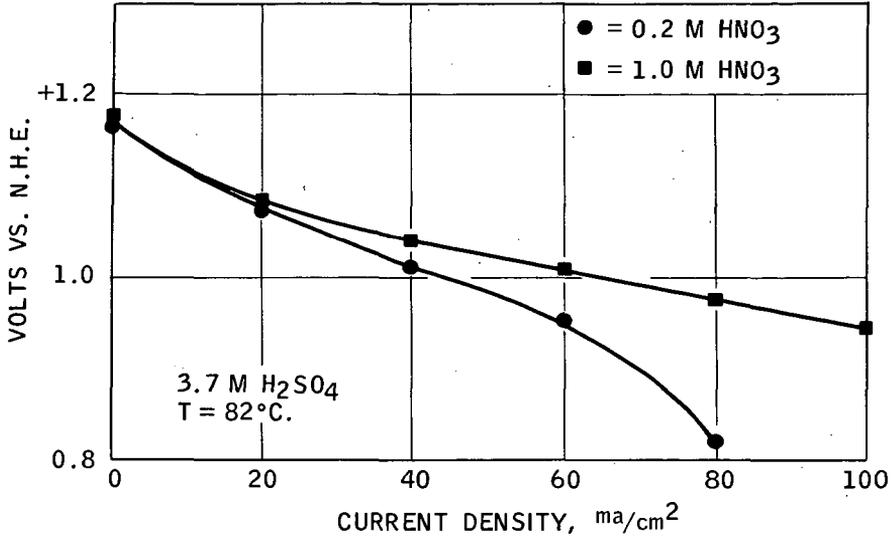
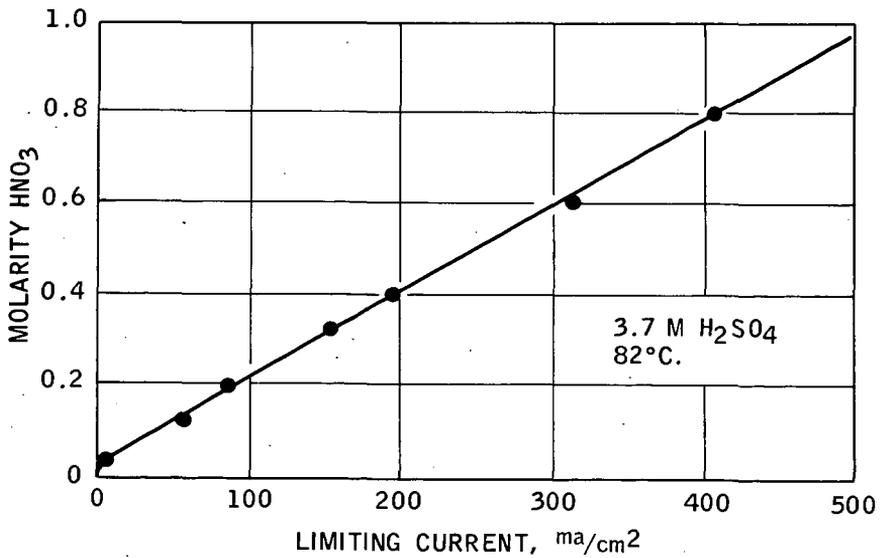
ACKNOWLEDGEMENT

This research is part of the Energy Conversion Project sponsored by the Advanced Research Projects Agency, Department of Defense. The contract, DA 36-039 SC-89156, was administered by the United States Army Electronics Research and Development Laboratory.

Some of the data presented was obtained by Esso Research and Engineering Company prior to the inception of this contract. The authors wish to acknowledge the efforts of their colleagues who contributed to this work, in particular Dr. A. W. Moerikofer, and to express their appreciation to Esso Research and Engineering Company for permitting its publication.

BIBLIOGRAPHY

- (1) Stein, B. R., "Status Report On Fuel Cells", p. 60-62, O.T.S. PB 151804 (1959)
- (2) Reneke, W. E., "Air Regeneration Of Bromine-Bromide Fuel Cell Catholyte" O.T.S. AD 273299 (1961)
- (3) Minc, S. and Jasielski, S., *Roczniki Chem*, 28, 109 (1954)
- (4) Ellingham, H. J. T., *J. Chem. Soc.*, 1565 (1932)
- (5) Monk, R. G., and Ellingham, H. J. T., *J. Chem. Soc.*, 125 (1935)
- (6) Vetter, K., *Z. physik. Chem.*, 194 199-206 (1950)
- (7) Delahay, P., "New Instrumental Methods In Electrochemistry", p. 184 New York, Interscience Publishers, (1954)
- (8) Beinert, H., and Bonhoeffer, K. F., *Z. Elektrochem. u. angew. physik. Chem.* 47, 538 (1941).
- (9) Chilton, T. H., "The Manufacture Of Nitric Acid by the Oxidation of Ammonia", *Chem. Eng. Progress Monograph*, No. 3, Vol. 56, A.I.Ch.E. (1960)

Figure 1 - Typical Performance Of HNO₃ Oxygen ElectrodeFigure 2 - Dependence of Limiting Currents on HNO₃ Concentration

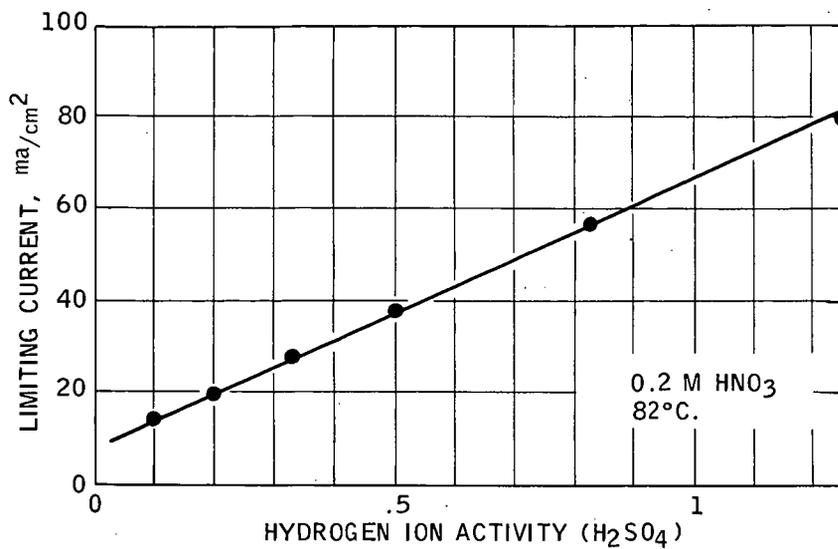


Figure 3 - Dependence of Limiting Currents on Hydrogen Ion Activity

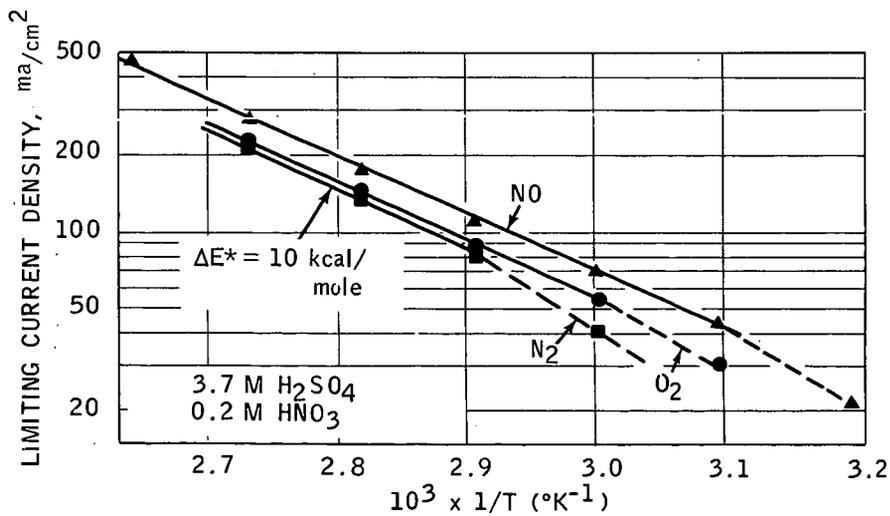


Figure 4 - Temperature Dependence of Limiting Current

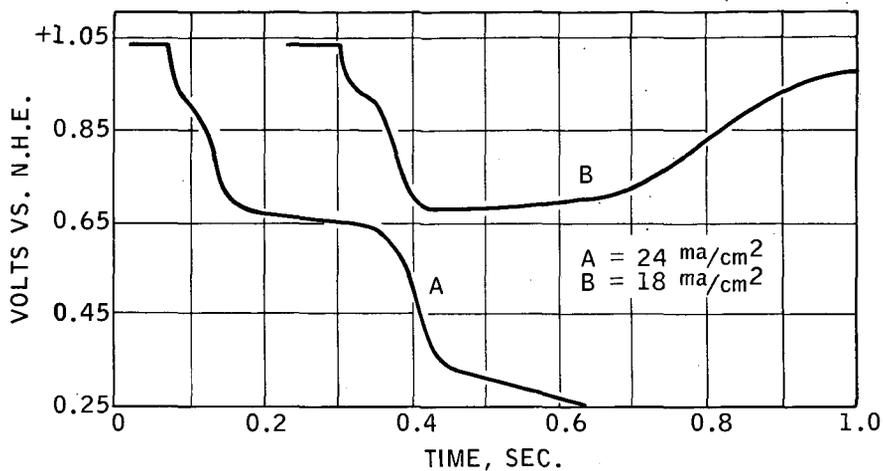


Figure 5 - Typical Voltage Transients at Constant Current

- A. Current in Excess of Limiting Current
- B. Current Less Than Limiting Current

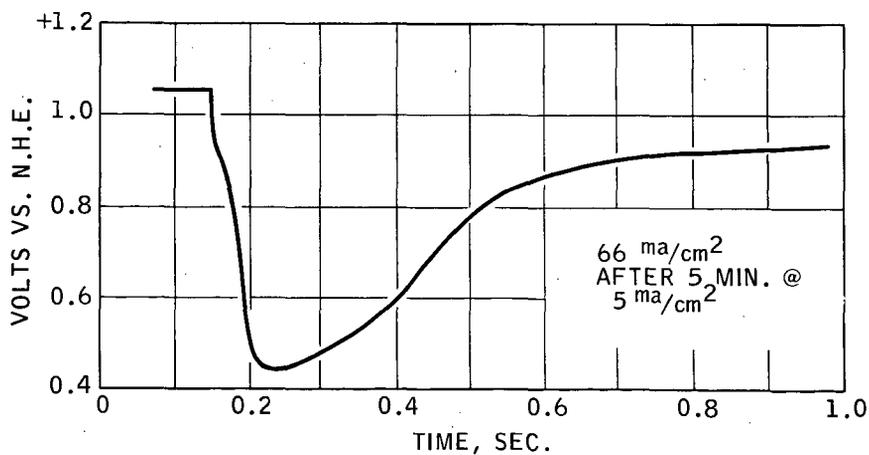


Figure 6 - Response to High Loads After Preconditioning

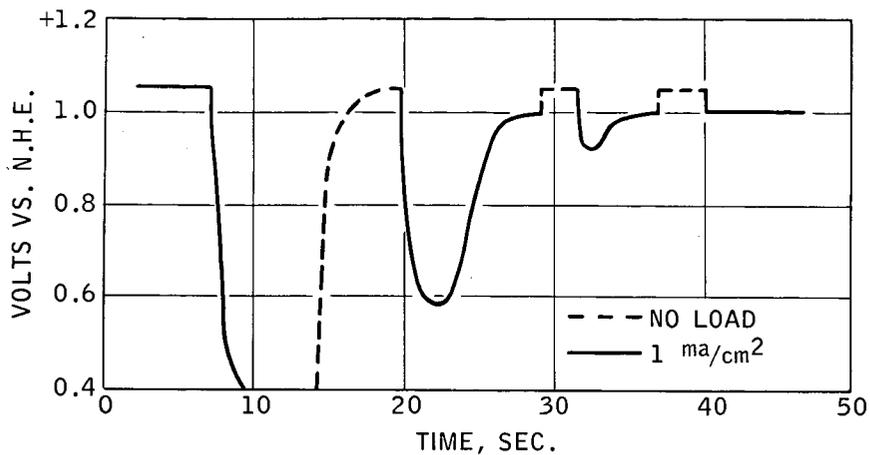


Figure 7 - Response to Repetitive Load

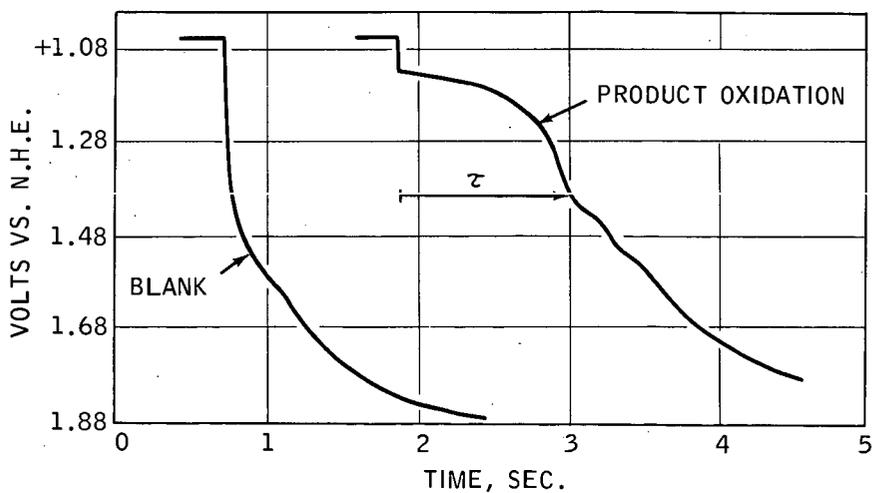


Figure 8 - Transient Observed During Product Reoxidation

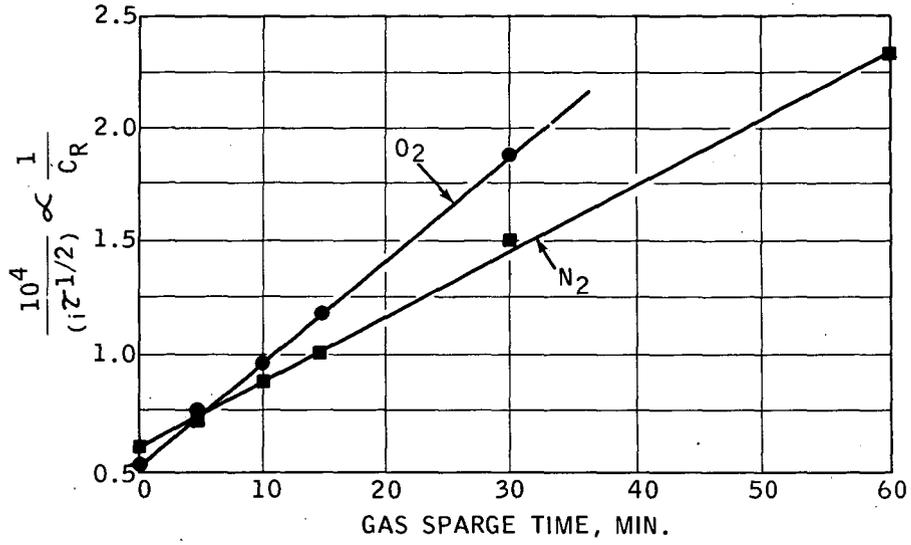


Figure 9 - Removal of Product by Gas Sparging