

REDOX STATE SENSOR TECHNOLOGY IN MOLTEN GLASS

FINAL REPORT

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ABSTRACT

This report covers an evaluation of the feasibility of a 3-wire cyclic voltammetric analytical method for the determination of the redox state of molten glass. The project was funded May 1, 1999 and was completed on Sept. 30, 2000.

INTRODUCTION

Considerable time and energy savings can be achieved in the glass industry if the redox state, primarily Fe (II)/Fe (III), of molten glass could be determined in-line. There is a similarity for an in-line redox sensing system for the glass industry to that of an electrochemical technique developed previously for the measurement of the uranium redox state in the Molten Salt Reactor project at Oak Ridge National Laboratory. If the Fe (II)/Fe (III) cyclic voltammetric wave is truly reversible, one could measure the ratio with a three platinum wire electrode assembly as was done in the reactor project. The process temperature in the glass industry is much higher, however, the electrochemistry should be the same.

There was, at the time of this project, no reliable technique for in-line determination of the redox state of molten glass at temperatures above 1400 °C, the temperature desired for preparation and processing of glass. Although there is a commercial technique for determining the redox state of glass up to 1300 °C, it is not necessarily an in-line approach. During the final review of this project in Oak Ridge on Sept.21-22, 2000 there was considerable discussion that there existed an in-line, referenced electrode commercial method for determining the redox potential in molten glass. That approach, however, was not a practical solution to the in-line needs; furthermore, the electrodes and reference had a very limited useful electrode lifetime at temperatures above 1400 °C .

BACKGROUND

A 3-wire cyclic voltammetric method for the determination of the U (III)/U (IV) ratio in operating molten salt nuclear reactors (1,2) had been developed previously by the author. It was successfully applied to both research and monitor reactor operation molten salts with the solution being essentially a LiF-BeF₂-ZrF₄-UF₄ melt in the temperature range of 500 to 700 °C. The advantages of the technique were that no reference electrode was required; no standard electrode potentials were needed to be utilized, and the results were independent of electrode area as long as signal could be observed. The electrode system consisted of three

platinum wires. One being a quasi-reference electrode that established some stable, but not necessarily known, potential in the melt; no current flowed in this electrode. The second and third wires were the small diameter indicator electrode and a larger counter electrode. Current was passed through these electrodes, and the current was plotted as a function of applied, and cycled voltage. For reversible electrochemical processes, the ratio of reduced to oxidized species could be determined by either measuring the ratio of the reduced to oxidized voltammetric signals or measuring the shift of the voltage of the redox couple from the potential of the quasi-reference platinum electrode. The potential of the quasi-reference electrode replaced the need for a known reference potential.

PROJECT CHRONOLOGY

A furnace capable of 1700 °C operation was obtained from the Metals and Ceramics Division and all high temperature experimental work was done in that facility. It was found that borosilicate glass could be melted and maintained in that furnace at temperatures up to 1500 °C. Initially the molten glass crept up the 99.9 % Al₂O₃ crucible in which it was contained. By using a longer cylindrical crucible it was possible to maintain the order of a 100 g glass melt without loss.

A three-wire platinum electrode assembly was prepared consisting of a 1 mm length of a 0.3 mm dia. (semi-micro) indicator platinum electrode incased in a 2 mm dia. 99.9% pure aluminum oxide tube. On either side of the outside of this tube, there was a 2.5 mm platinum counter electrode and a 2.5 mm platinum quasi-reference electrode. The three electrodes were separated by the aluminum oxide tube and the exterior wires were held on the outside of the tube (and separated from each other) by an aluminum oxide based (alundum) cement. Both the counter and quasi-reference wires were exposed to the full height of the melt. The assembly is shown in Figure 1.

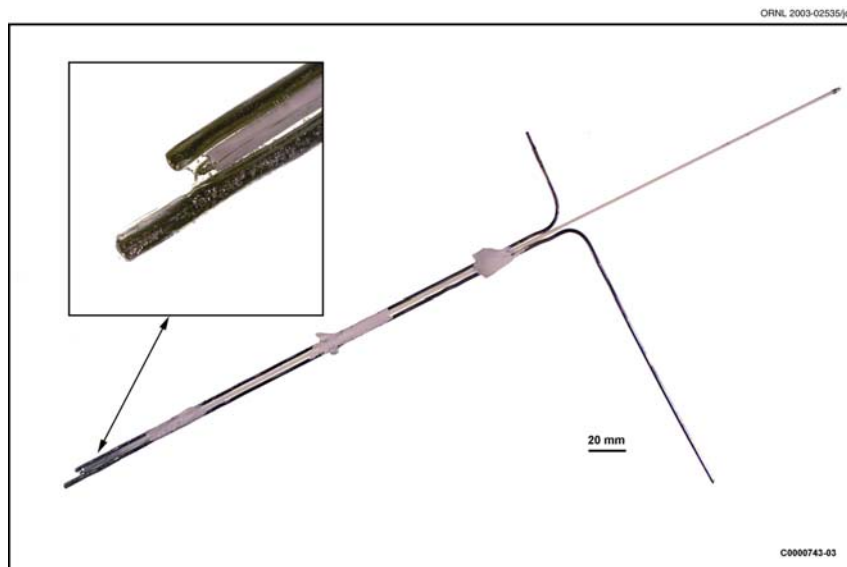


Figure 1. Redox electrode assembly

The operation of the assembled three-wire electrode system was verified by obtaining cyclic voltammograms (CV) of aqueous potassium ferri-ferro cyanide solutions. These experiments were carried out using a Perkin Elmer, Model 263a, potentiostat. Operation was deemed quite acceptable and a representative CV is shown in Figure 2. As noted in the figure, however, the CV was obtained versus a saturated KCl reference electrode to verify the voltage of the voltammetric wave. The curve shows an expected wave for the reduction and oxidation in a reversible Fe (II)/Fe (III) electrode reaction. That shape is ideally what would be expected of a reversible electrochemical process.

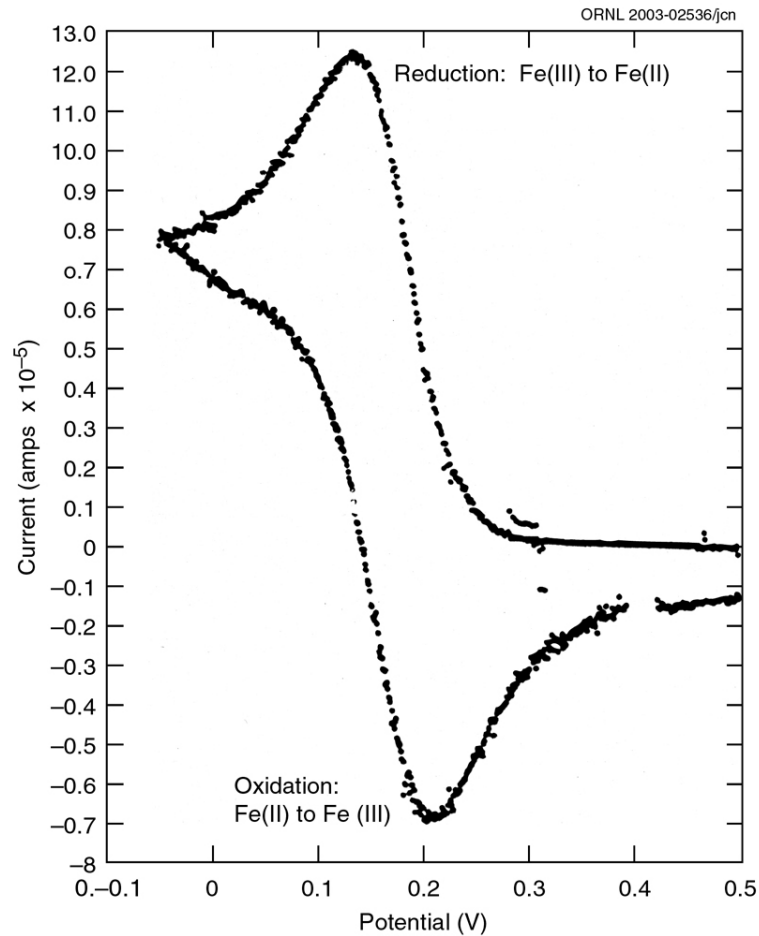


Figure 2. Cyclic Voltammogram of Fe(II)/Fe(III) in aqueous solution at 25 °C using a saturated KCl reference electrode

For the remainder of this study, a glass specimen supplied by PPG and containing approximately 500 ppm Fe was used. The first CV's were carried out over a voltage range of -1.0 to $+0.5$ volts and essentially included the cathodic (negative) and anodic (positive) voltage limits of the melt. The scan rate was 50 V/sec. An example of these results is shown in Figure 3. The scan indicates a reduction of Fe(III) to Fe(II) at about -0.3 volts. This potential is similar to that reported by others in silicate melts (3). As the voltage scanned toward more negative voltage, however, the electrode became erratic and was not useful. Probably, as the electrode was scanned to the more negative potentials, Fe(II) was further reduced to Fe metal which alloyed with the platinum electrode. The electrode then was no longer functional. Thus no further experiments were carried out at the voltage limits of the molten glass.

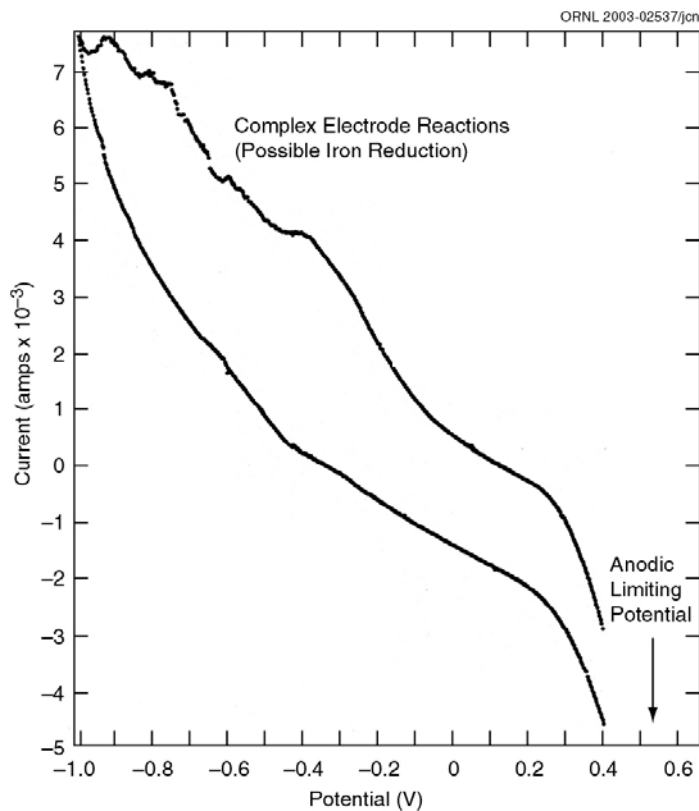


Figure 3. Cyclic Voltammogram of Fe(II)/Fe(III) in molten glass at 1450 °C (quasi-platinum electrode – potential scanning to anodic limit damages sensor)

An example of the final experimental results is shown in Figure 4. Reproducible CV's were obtained at scan rates of 100V/sec using a fresh indicator electrode replacing the electrode that was poisoned by Fe metal reduction and with scan limits set to avoid the solvent cathodic and anodic limits. Note in this figure that a smooth scan is seen with a reduction wave near -0.3 volts and a corresponding oxidation near -0.1 volt. This CV is not as well-defined as the CV shown in Figure 2, however, it does show the reversible character necessary for an in-line redox application. The work to this point was presented at the "FY 2000 Glass Industry Project Review held in Oak Ridge, Sept. 21-22, 2000.

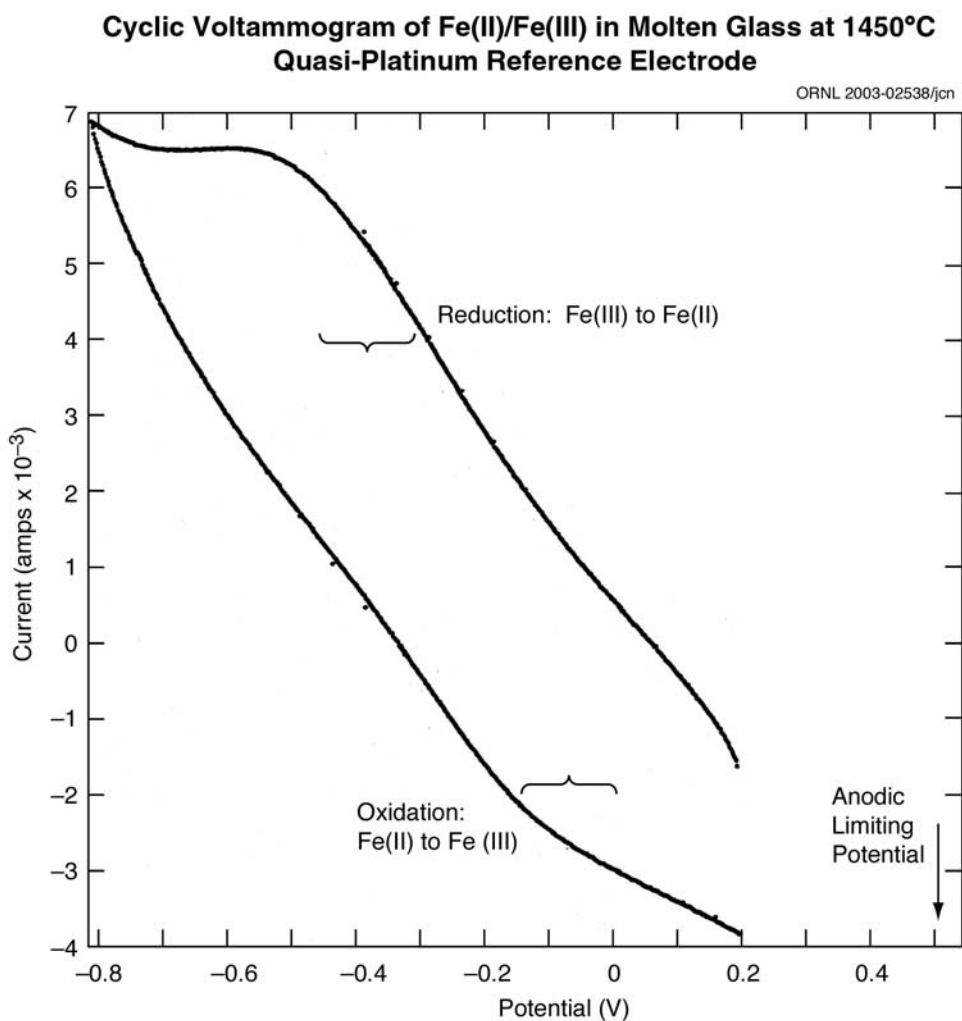


Figure 4. Cyclic Voltammogram of Fe(II)/Fe(III) in molten glass at 1450 °C – quasi platinum electrode.

SUMMARY

Progress was made toward showing the feasibility of the use of a 3-wire CV as an in-line redox measurement method for use in molten glass. The initial objective of the project was to investigate the feasibility of such a technique for the above measurement. The feasibility was demonstrated at 1450 °C. A successful field-usable application would, however, be several years in the future as more research and development would be required.

There are several additional topics that would need to be considered in order to lead to an implementation of the technology. A semi-micro indicator electrode was chosen for this study. In reviewing the results, it seems that a smaller, micro, electrode would need to be developed as too much current was drawn by the 0.3 mm dia. electrode that was used. A more rugged electrode assembly would also be required than was used in the laboratory. Minor corrosion of the aluminum oxide insulating rod was observed. The corrosion would have required periodic replacement of the electrode or some arrangement to remove and reposition the assembly for long term use. Finally, investigation of the reason(s) for the electrode failure at the solvent potential limits would be necessary for a functional application of the technology to be successfully implemented.

REFERENCES

1. Mamantov, G. and Manning, D.L., Anal. Chem., 38, (1966) 1494
2. Molten Salt Reactor Semiannual Report, Feb. 28, 1969, p 201. ORNL-4396
3. Schreiber, H.D., Wilk, N.R. Jr., Schreiber, C.W., Proc. 18th Intl Cong. On Glass, 1988

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