N90-20471

CORROSION TESTING OF CANDIDATES FOR THE ALKALINE FUEL CELL CATHODE

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Current/voltage data have been obtained for specially made corrosion electrodes of some oxides and of gold materials for the purpose of developing a screening test of catalysts and supports for use at the cathode of the alkaline fuel cell. The data consist of measurements of current at fixed potentials and cyclic voltammograms. These data will have to be correlated with longtime performance data in order to fully evaluate this approach to corrosion screening.

INTRODUCTION

Preliminary screening of materials intended for oxygen reduction performance electrodes for the alkaline fuel cell is desirable in order to minimize the number of long term test electrodes that might otherwise be required. Moreover, a section from a performance electrode would not be as satisfactory as a specially made corrosion electrode for this purpose because the latter should be made much more wettable and intended for submersion in the electrolyte.

EXPERIMENTAL

1. Materials

$NiCo_2O_4$ spinel was synthesized by co-precipitation, in the manner of Tseung and Botejue (1985). This material was characterized in Singer et al (1987); its surface area is 70 m^2/g. The pyrochlore $Pb_2Ru_2O_{6.5}$ was synthesized after the method of Horowitz (1978, 1983); its surface area is 101 m^2/g. Two gold standards, or blanks, were employed. One was the gold wire screen used as the substrate for the oxides; the other was a piece from an actual working electrode as used in Orbiter fuel cells, comprising 20 mg/cm^2 of Au-10% Pt of surface area 12 m^2/g and about 30 wt % PTFE (Teflon).

2. Electrode Fabrication

Pure Au wire screen was the substrate in the oxide electrodes. The screen was 50 mesh, of 0.25 in. wire; approximately 0.5 cm^2 surface area of wire was included in the submerged part of the oxide electrodes whose loadings were about 25 mg/cm^2. The IFC Orbiter electrode yielded a BET surface area of 2000 cm^2 in the electrode.

3. Measurements

4 mm x 10 mm rectangular cuts of the fabricated electrodes were microtorch spot welded to the 0.020 inch gold wire lead with a 4 mm x 2 mm piece of Au foil enfolding the clear area of the electrode and the wire. The contacted electrode was immersed in the floating half-cell of Giner (1967) within the cylindrical cage into which the reference electrode faces (Fig. 1). The immersion included all the active material and a minimum of the clean gold above it. The Teflon bracket of the half-cell shown in Figure 1 which is used to contact the dry side of working electrodes, was completely removed. The electrolyte was 30% KOH, the counter electrode was Pt or Au foil, and N_2 with about 1 ppm O_2 was passed through a 30% KOH bubbler before the cell. Most measurements were made at 24^{o} C. Stirring was found to be detrimental.

Currents at fixed voltages were measured with a PAR 173 potentiostat with a 376 attachment leading into a recorder or a voltammeter. The O_2 reduction range between 1.0 and 0.6v (RHE) was of most interest for observing corrodibility, although some data were taken beyond these limits.

RESULTS

The current obtained from the gold wire screen, which was used as the collector-substrate for all the materials except the IFC electrode, is shown in Figure 2. The rapid drop to a steady current of a few microamps is noted. The log-log plot was found generally useful for extrapolation to long times.

The IFC Au-Pt electrode, based on a pure gold wire screen of denser mesh than used in the other electrodes, required a longer time to fall to the same microamperage than required by the bare gold wire (Figure 3). Figure 4 shows the more rapid fall to a lower current for the same electrode at 0.6v than at 0.3v.

The cyclic voltammograms of Figures 5 and 6 show appreciable differences between the bare gold wire and the Orbiter teflonated gold electrode.

Corrosion currents obtained with the Pb-Ru pyrochlore and the Ni-Co spinel electrodes are shown, respectively, in Figures 7 and 8. Cyclic voltammograms for these two specimens are given in Figures 9, 10, and 11.

DISCUSSION

The final currents obtained with the two gold standards are of the order of microamps. It may be assumed that most of this is due to trace O_2 in the environment. The IFC electrode may be expected to be most efficient at reacting with trace O_2, having been optimized as a porous hydrophobic-backed reduction electrode. Perhaps another type of gold electrode standard could be envisaged, namely a corrosion type designed for maximum wetting, using pure Au colloid and minimum Teflon.

The cyclic voltammograms of the gold specimens show sensitivity to absorption of trace oxygen species at 0.926v (RHE) = 0 volts (Hg/HgO); the IFC electrode plainly shows, in addition, its Pt content, in its resemblance to Pt cyclic voltammograms throughout the literature (Will, 1966). The sharp rise in current above 500v (Hg/HgO) is due to O_2 evolution, which itself would supply O_2 to both gold electrodes in addition to the ca. 1 ppm in the N_2 gas supply, and to back diffusion and leakage of air. In summary, the very low currents rapidly obtained in Figures 2, 3, and 4 indicate a satisfactory standard for relative non-corrodibility.

The pyrochlore used in this work is part of a study to make an improved material with the expectation of improving its stability reproducibly. Whether the present data indicate progress in this direction cannot yet be stated; however, Figures 7, 9, and 10 obtained with this pyrochlore synthesis show no drastic corrosion, in agreement with Horowitz (1983). This surmise is fortified by comparison with the spinel data of Figures 8 and 11. $NiCo_2O_4$ has been reported to be unstable to reduction potentials (King and Tseung (1974) which is one reason it was used in this study. During the performance represented by Fig. 8 a black coating developed on the counter electrode. This was dissolved in HCl. Ni and Co were found, with about 6 times as much Co as Ni; however, no attempt was made to relate this finding quantitatively to the corrosion data.

Comparisons of corrosion tests, like these reported, with longtime performance electrode tests, will have to be made to evaluate this type of screening. The present preliminary work suggests that this approach is worth pursuing.

CONCLUSIONS

Corrosion test screening of candidates for the oxygen reduction electrode of the alkaline fuel cell has been applied to two substances, the pyrochlore $Pb_2Ru_2O_{6.5}$ and the spinel $NiCo_2O_4$. The substrate gold screen and a sample of the IFC Orbiter Pt-Au performance electrode were included as blanks. The pyrochlore data indicate relative stability, although nothing yet can be said about long term stability. The spinel was plainly unstable. For this type of testing to be validated, comparisons will have to be made with long term performance tests.

Acknowledgement

The collaboration of PSI Technology Company of Andover, MA, under Contract NAS3-25199, in the preparation of the oxides and their electrodes used in this study is herewith acknowledged. The provision of a sample of Orbiter electrode by Dr. Ron Martin of IFC is gratefully acknowledged.

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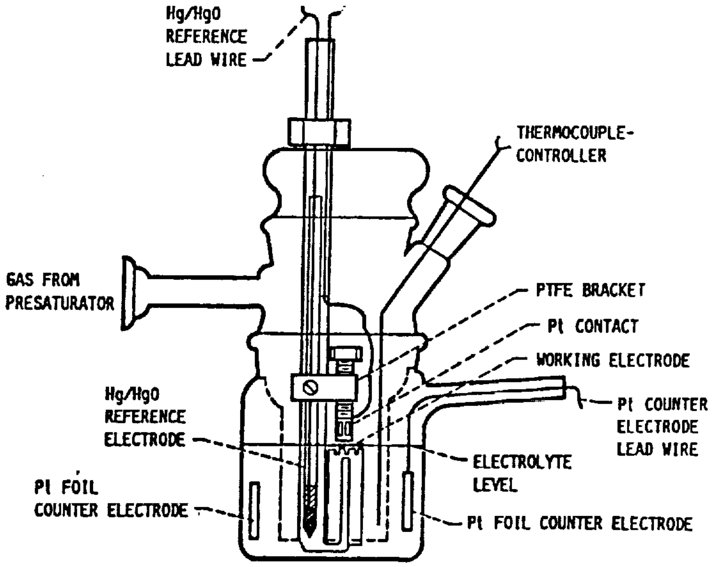
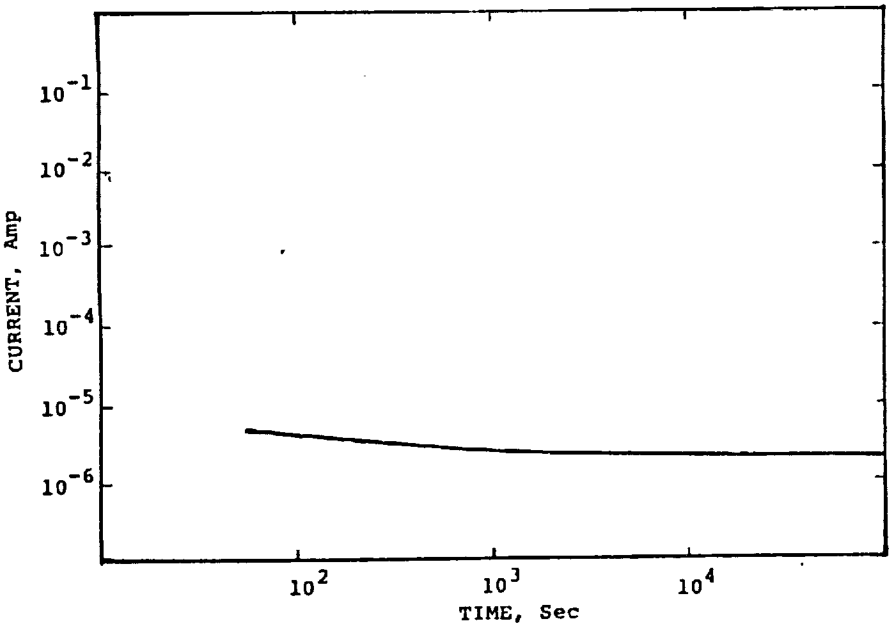
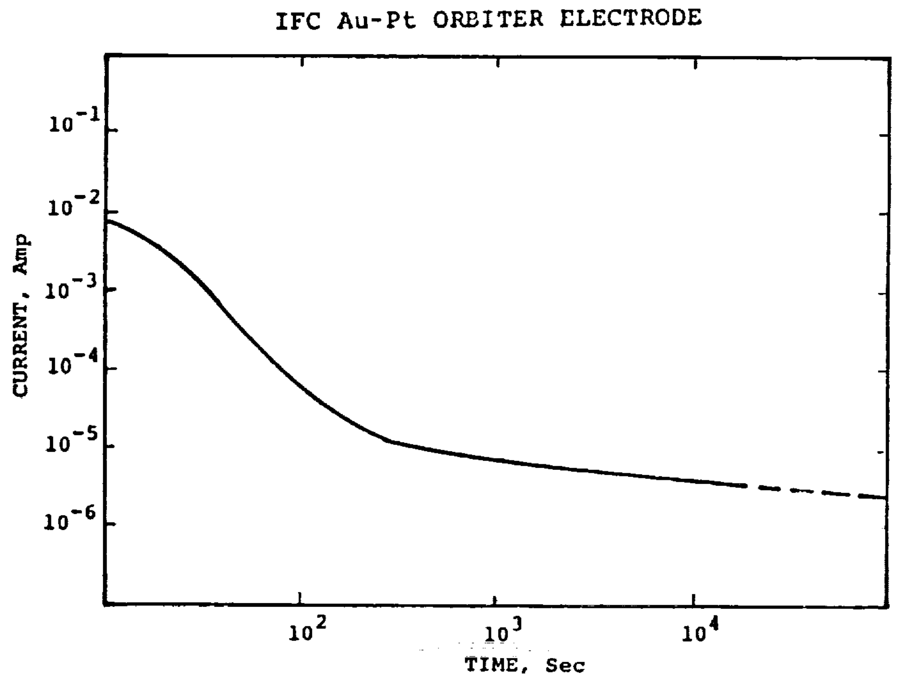


FIG. 1. FLOATING HALF-CELL



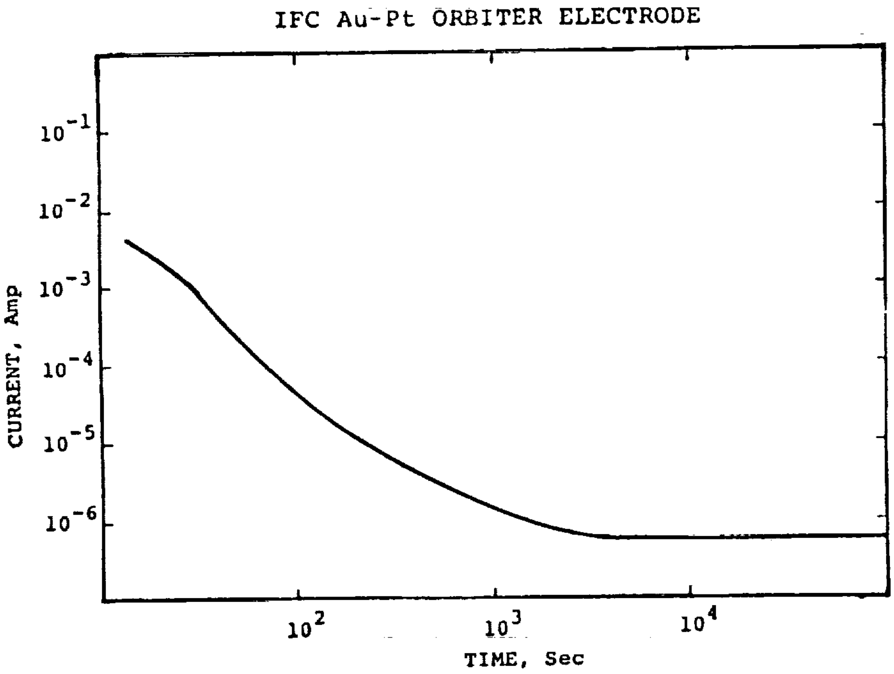
Gold Wire Screen 0.300 V(RHE); 24 deg C

FIG. 2. CORROSION CURRENT



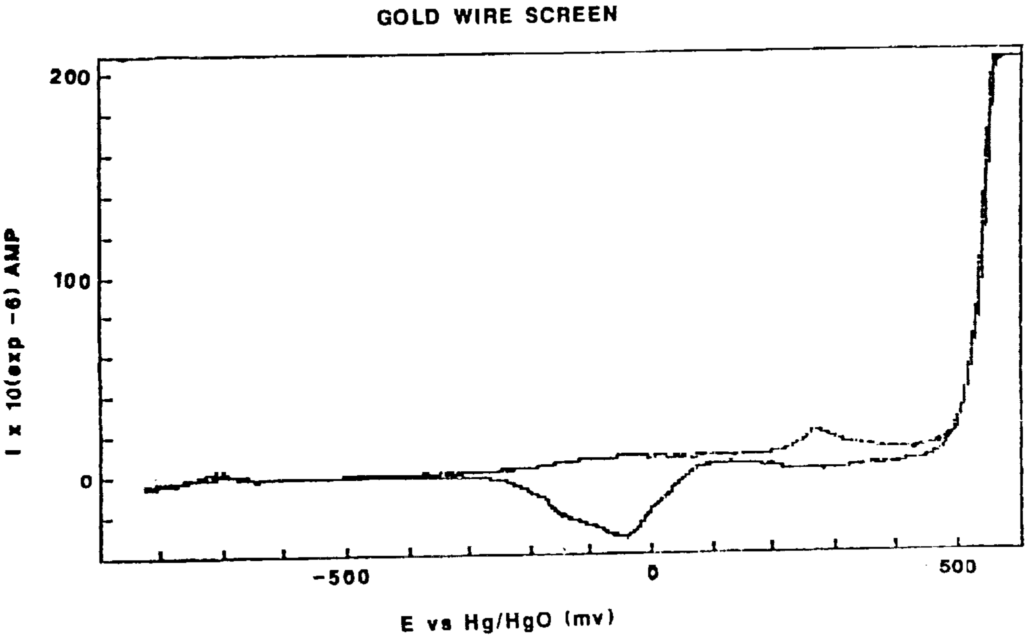
0.300 V(RHE); 24 deg. C

FIG. 3. CORROSION CURRENT



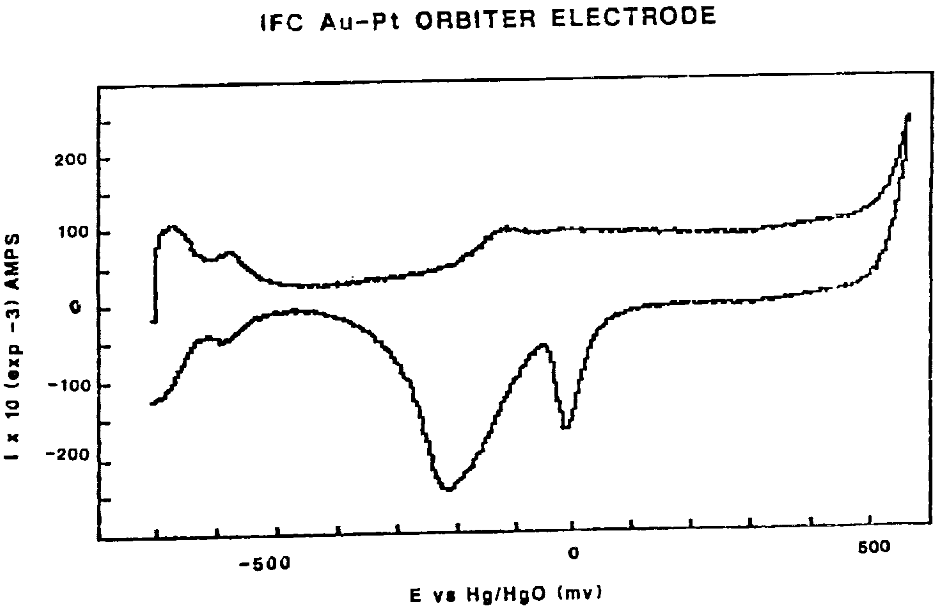
0.600 V(RHE); 24 deg. C

FIG. 4. CORROSION CURRENT



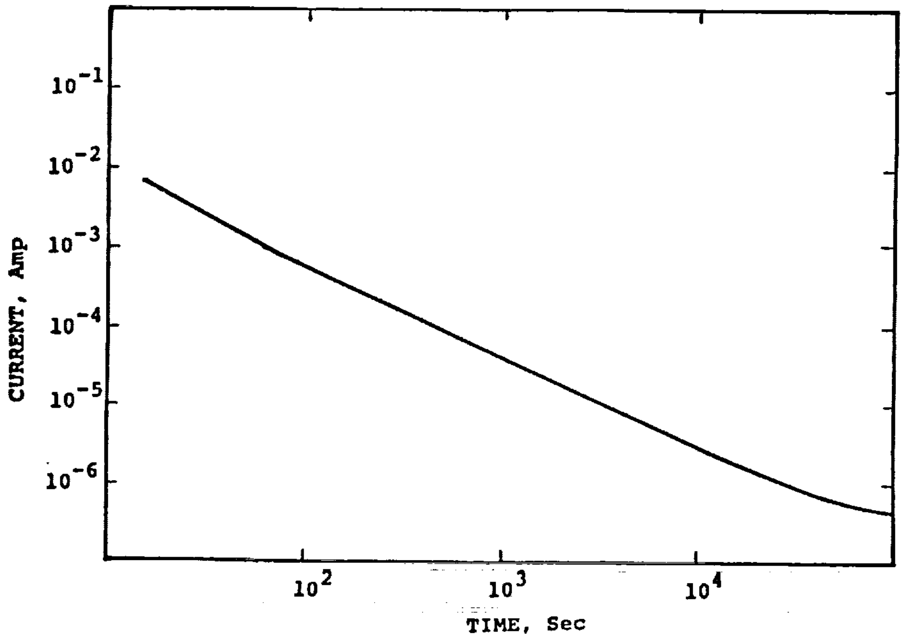
Sweep: 600 to -826 mv, 1 mv/s, 80 deg. C, Nitrogen, 30%KOH

FIG. 5 CYCLIC VOLTAMMOGRAM; GOLD WIRE SCREEN



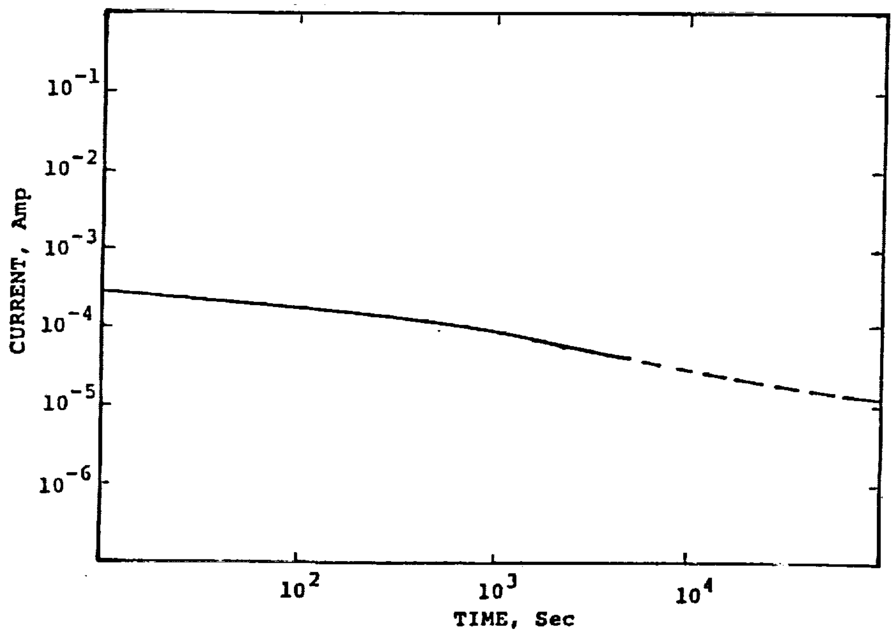
Sweep: 564 to -706 mv, 1 mv/s, 24 deg.C, Nitrogen, 30%KOH

FIG. 6 CYCLIC VOLTAMMOGRAM


PSI Pb-Ru PYROCHLORE CORROSION ELECTRODE

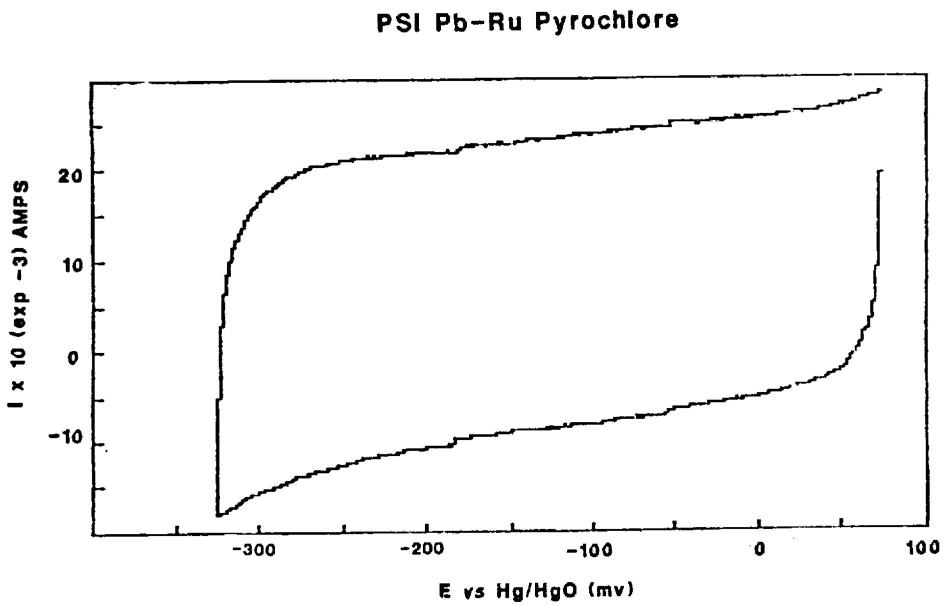
0.700 V(RHE); 24 deg. C

FIG. 7 CORROSION CURRENT


PSI Ni-Co CORROSION ELECTRODE

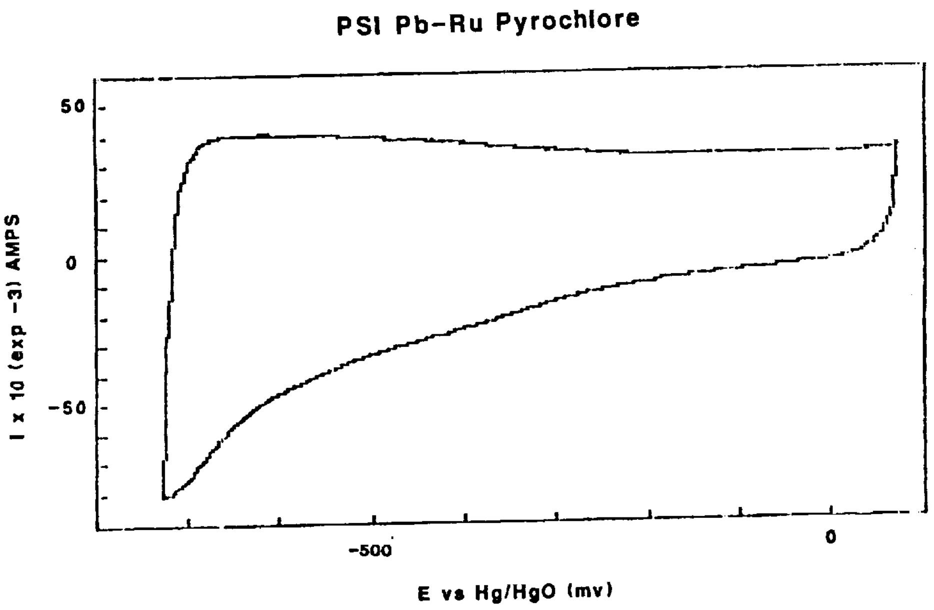
0.600V(RHE); 24 deg. C.

FIG. 8 CORROSION CURRENT



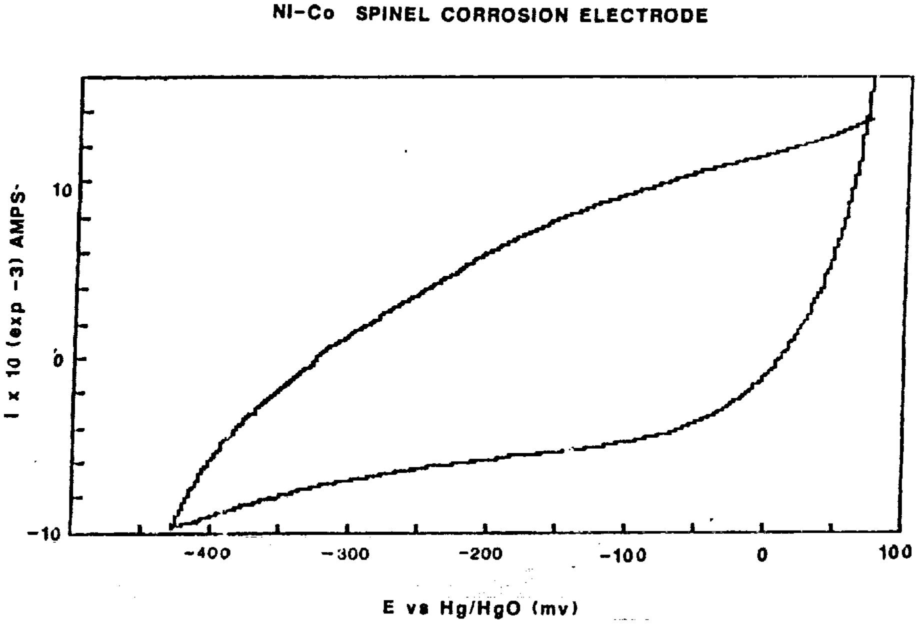
Sweep: 74 to -326 mv, 1 mv/s, Nitrogen, 30% KOH

FIG. 9 CYCLIC VOLTAMMOGRAM



Sweep: 74 to -726 mv, 1 mv/s, 24 deg. C, Nitrogen, 30% KOH

FIG. 10 CYCLIC VOLTAMMOGRAM



Sweep: 74 to -326 mv,80 deg. C, Nitrogen, 30% KOH

FIG. 11 CYCLIC VOLTAMMOGRAM