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IMPEDANCES OF ELECTROCHEMICALLY IMPREGNATED NICKEL ELECTRODES AS FUNCTIONS OF POTENTIAL, KOH CONCENTRATION, AND IMPREGNATION METHOD

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INTRODUCTION

Nickel-cadmium cells have long been used in batteries for space satellites, and nickel-hydrogen cells are starting to replace these, both in geosynchronous (GEO) and low-earth orbit (LEO) spacecraft. The cycle life and depth-of-discharge requirements for geosynchronous orbit can be readily met, but the requirements for LEO operation are much more stringent. Nickel-hydrogen batteries will be used in Space Station Freedom, which will require very long cycle lives of at least 30,000 cycles at 35% depth of discharge. In this cell, the life-limiting factor is almost always the nickel electrode. Impedance spectroscopy is being investigated as a means of determining the failure modes of nickel electrodes and a possible means of differentiating between good and bad electrodes and cells at an early stage of life. This method allows a number of electrode parameters to be determined simultaneously and is also a method that can be used for in-situ, non-destructive study of electrodes and cells over a wide range of cell and electrode sizes.

Many impedance studies have been carried out on nickel electrodes and Ni/Cd and Ni/H_2 cells. Some studies have been made while the cells or electrodes were being discharged (Ref. 1), others at various equilibrium voltages or states of charge (Refs. 2-8). The impedances have been found to be strongly dependent on the state of charge and/or voltage and on the procedure used to obtain the measurements. The studies have been similar qualitatively but not quantitatively. In order for impedance to be used as a diagnostic tool and for quantitative comparisons to be made, more reproducible measurements are necessary.

As part of a study of loss of capacity in Ni/H_2 cells for space use (Ref. 9), electrochemically impregnated nickel electrodes for Ni/H_2 cells (3.5" diameter) were obtained from the four U.S. manufacturers and cycled until the capacity was stable. Impedance measurements were then made in both the usual 31% KOH electrolyte and in 26% KOH, since recent studies have indicated that the latter electrolyte can increase the life of the Ni/H_2 cells by as much as a factor of ten. Impedance spectra of several electrodes were measured as a function of voltage to determine the optimum voltages for comparison. At high states of charge the impedances are very low and do not vary much from electrode to electrode while at low states of charge there are often large difference between electrodes. Therefore, the impedances of the electrodes were measured at a voltage corresponding to a very low state of charge in order to capitalize on these differences. One-third of the electrodes were also measured in the charged state. Large differences were observed at the lower voltages between the electrodes from different manufacturers, and small differences between individual electrodes from the same manufacturer. Differences were also seen between the electrodes in 26% KOH and 31% KOH. The full significance of these

results is not yet clear, but the results seem to correlate with preliminary data from life testing of full-size cells.

EXPERIMENTAL

The initial measurements of impedance as a function of voltage and the measurements on the individual electrodes at the comparison voltages were made using the Princeton Applied Research (PAR) M378 Impedance System using a PAR model 5208 Lock-in Analyzer and a PAR Model 273 Potentiostat/Galvanostat. More detailed measurements as a function of voltage were later made using the Solartron 1250 Frequency Response Analyzer and the Solartron 1286 Electrochemical Interface.

Fifteen electrodes were obtained from each of four U.S. manufacturers: Gates Aerospace Batteries, Whittaker-Yardney, Hughes, and Eagle-Picher (Joplin, MO). Twelve electrodes from each manufacturer were cycled in 31% KOH, three in 26% KOH. The electrodes were given six to seven cycles of formation cycling at an estimated C/10 rate followed by discharge at a C/5 rate to 1.00 V vs an amalgamated zinc reference electrode. The preliminary capacities determined from the formation cycling were then used to determine the currents for the final determination of capacity. In these measurements the electrodes were cycled at a C/2 charge rate and discharged at a C/4 rate for five to six cycles to 1.00 V vs the amalgamated zinc reference. It was more convenient to use amalgamated zinc electrodes than Hg/HgO electrodes for the formation cycling and capacity determination since fifteen electrodes were being cycled simultaneously. However, Hg/HgO electrodes were used for the impedance measurements since this is a more stable reference electrode. The voltage at which the discharge was terminated during the cycling (1.00 V vs the zinc electrodes) corresponds to about -0.41 V with respect to the Hg/HgO reference electrode used in the impedance measurements. After the final discharge, the electrodes were equilibrated at 0.200 V vs the Hg/HgO reference electrode for an hour before the impedance measurements. One-third of the electrodes were also partially charged and equilibrated for an hour at 0.400 V before measurement at that potential. (The state of charge at 0.200 V is about 1% and that at 0.400 V is between 9 and 18%, depending on the manufacturer and the concentration of KOH).

RESULTS AND DISCUSSION

The impedances were analyzed assuming a simple circuit as shown in Figure 1 (Ref. 10). For a planar electrode, the diameter of the semicircle in the complex plane plot is the kinetic resistance, and the slope of the Warburg plot (Z_{real} vs $\omega^{-1/2}$) is inversely proportional to $CD^{-1/2}$ where C is the concentration of the diffusing species and D is the diffusion coefficient. There is as yet no adequate theoretical treatment of the impedance of a porous electrode with insoluble reactant species such as the nickel electrode. However, the impedance curves for porous electrodes have the same general shapes as the curves for planar electrodes, so we will analyze them in the same way. The kinetic resistances and Warburg slopes that we obtain will be valid empirical numbers for comparison of different electrodes, but in the absence of a theoretical treatment we cannot calculate the true exchange currents, diffusion coefficients, or concentrations of diffusing species.

Figures 2 and 3 give some typical data for impedance as a function of voltage for an electrode from Gates Aerospace Batteries plotted in the Bode representation. In order to get reproducible measurements it was necessary to begin with fully-charged electrodes. For this set of experiments, the voltage was lowered in increments, and electrodes were held overnight at each potential to stabilize them. It can be seen from Figure 2 that as the voltage is decreased, the magnitude of the impedance rises by several orders of magnitude at the lower frequencies. However, at -0.927 V vs the Hg/HgO electrode (corresponding to the potential of the hydrogen electrode, i.e., the potential of a short-circuited cell), the impedance decreases at the lower frequencies. This may be due to the reduction of a small fraction of the hydroxide to metal atoms or clusters which reduce the kinetic resistance and increase the rate of diffusion. Further study is needed to clarify this phenomenon.

In a simple RC circuit such as shown in Figure 1, a single minima is produced in the Bode angle plots. The data in Figure 3 indicate that there are at least two overlapping minima, thus more than one RC circuit is needed to fully model the data. One possible alternative circuit is given in Figure 4. More accurate measurements of the impedance as a function of voltage are now under way, and the data are being analyzed in terms of this model and others.

Nyquist plots of some of the higher frequency data are given in Figure 5 showing the increase in kinetic resistance as the voltage is lowered, in particular at the lower voltages. The Warburg plots in Figure 6 illustrate the increase in slope as the voltage is lowered. The $CD^{-1/2}$ term is thus decreasing as the voltage becomes lower, signifying an increased resistance to diffusion. The data shown in these figures is for the voltage range where the greatest changes in impedances occur as the voltage is lowered.

Electrodes from other manufacturers show similar changes with voltage, but the results differ quantitatively. Apparently slight differences in the method of preparation and formation of the electrodes are significant, which explains why impedance measurements from different researchers vary significantly. It was found that impedances measured in the range of 0.325 V to 0.175 V vs Hg/HgO not only showed the greatest changes with voltage but also provided the greatest differentiation between electrodes from different manufacturers. These voltages correspond to very low states-of-charge. At higher voltages the impedances are very low, and there are only small variations between electrodes from different manufacturers. Impedances at voltages lower than 0.175 V are larger, but equilibration times are longer and the scatter is much greater. A voltage of 0.200 V was chosen for the comparisons between the electrodes from different manufacturers. (Measurements were also made at 0.400 V, but at this voltage the impedances are much smaller and the differences between the electrodes from the four manufacturers are negligible, so the data are not presented here).

These voltages can be converted to the standard hydrogen electrode potential scale in the same KOH concentration by adding 0.926 V, the difference between the standard potential of the hydrogen electrode in basic solution and that of the Hg/HgO electrode (Ref. 11). The relationship of these voltages to voltages in real Ni/H_2 cells is not exact, due to several factors. Thus a voltage of 0.200 V for the nickel electrode vs the Hg/HgO electrode would correspond to a voltage of 1.126 V vs a hydrogen electrode at 1 atm. pressure. However, in Ni/H_2 cells the hydrogen pressure varies over the course of the

charge-discharge cycle and will affect the voltage of the hydrogen electrode and thus the cell voltage. A typical pressure for a new Ni/H_2 cell in the discharged state is about 50 PSIG (4.40 atm.). (The pressure is about 600 PSIG in the fully charged condition). When the nickel electrode is 0.200 V vs Hg/HgO, the electrode is almost fully discharged, so the correction to the hydrogen electrode and cell voltage because of the increased hydrogen pressure is about 19 mV. This means that a nickel electrode voltage of 0.200 V vs the Hg/HgO electrode is equivalent to a final voltage of about 1.145 V vs the hydrogen electrode in a typical Ni/H_2 cell. The corresponding voltage for a Ni/Cd cell is 1.107 V.

An additional difficulty in comparing potentials in a real cell with those relative to the Hg/HgO reference electrode is the effect of changes of concentration of KOH and H_2O. During discharge of a Ni/H_2 cell, hydroxide ions are produced at the nickel electrode and consumed at the hydrogen electrode. Water is consumed at the nickel electrode and produced at the hydrogen electrode. In a Ni/Cd cell hydroxide ions are consumed at the Cd electrode. The concentration of KOH within the electrodes will therefore depend not only on the initial concentration added to the cell but will vary with the rate of discharge and the rate of diffusion of KOH and water into and out of the electrodes. This will affect the potentials of both electrodes to a small extent unless the system is equilibrated for sufficient time for all species to come to uniform concentrations. The effect of changes in KOH concentration will probably be much greater in a real cell where there is a minimal amount of electrolyte than in these beaker experiments against a Hg/HgO reference electrode where there a large excess of electrolyte. This effect cannot be corrected for but is a source of a small uncertainty.

Figures 7 and 8 are typical complex plane plots for the electrodes from the different manufacturers at 0.200 V. We observed small differences in electrodes from the same manufacturer, but differences between electrodes from different manufacturers are much larger. Impedances at 31% KOH are larger for the electrodes from Hughes than for the Eagle-Picher and Gates electrodes and much larger for the Whittaker-Yardney electrodes. In 26% the impedances of electrodes from Eagle-Picher and Yardney do not differ greatly from those in 31% KOH. The impedance of the Eagle-Picher electrode is still small and that of the Yardney electrode is still larger than the others. However, the impedance of the Gates electrode is much larger in 26% KOH; that of the Hughes electrode is much smaller.

The values for the average kinetic resistances and Warburg slopes for these electrodes are listed in Table 1 using the simplistic model shown in Figure 1. The values for the kinetic resistances for the Gates and Eagle-Picher electrodes are estimated, since these original measurements showed a great deal of scatter. More accurate measurements are now being carried out with more sensitive instruments.

In terms of cell performance, a larger kinetic resistance means than an electrode would have a greater kinetic polarization (overvoltage) than one with a lower kinetic resistance. Likewise, since a larger Warburg slope means that diffusion is slower, an electrode with a larger slope would have a greater diffusion overvoltage. Thus an electrode with a low kinetic resistance and a low Warburg slope would be expected to give better performance.

Limited cell tests that we have carried out in the past indicate a probable correlation between the impedance parameters and cell life and performance (Ref. 12). Cells from Yardney have had much shorter cycle lives at high depths-of-discharge, although they have had excellent cycle lives at low depths-of-discharge (higher voltages), where the impedance parameters are comparable to those of other manufacturers (Ref. 13). Boiler plate cells from Hughes using 26% KOH have shown much longer cycle lives than those cycled in 31% KOH, consistent with the lower impedance that we see in the 26% KOH (Ref. 14). These electrodes have a higher Co level than those from other manufacturers, and this may be responsible for the longer life in 26% as well as the lower impedance.

These results obviously are only applicable to electrodes manufactured under the same conditions as the electrodes examined in this study and with the same cycling history. Changes in manufacturing processes will change the impedances as well as cell performance. Although the nickel electrode is usually the dominating factor in the performance of the cell, other factors such as separators, electrolyte level, etc. will affect performance. Thus the impedance of the nickel electrode by itself will probably predict cell performance in most cases, but in some instances these other factors may predominate.

We are also examining the changes in impedance with cycling. The electrodes that were studied here had undergone formation cycling in the factory and were cycled sufficiently before the impedance testing to come to a stable capacity. The impedances of electrodes from each manufacturer were very similar, indicating that reproducible results can be obtained if electrodes are cycled in the same way. However, measurements on the 65 AH flightweight cells being tested for the Space Station Freedom and on several flightweight Ni/Cd cells indicate that gradual changes in impedance take place during early cycling even after a stable capacity is reached. Significant impedance changes apparently take place throughout the life of the electrode, not just late in its cycle life. In some cases the impedance seems to increase in the early stages of cycling and in other cases it decreases. Thus valid comparisons can only be made between cells or electrodes that have the same cycling history. In order to further understand the impedance of nickel electrodes, we are carrying out more detailed experiments on the impedances of these electrodes, not only as functions of manufacturer, KOH concentration, and voltage, but also as a function of cycle life. We are also following the impedances of the Space Station cells during their long-term cycling to failure at 35% DOD under a Low Earth Orbit cycling regime of 55 minutes charge followed by a 35 minute discharge. We expect the measurements on these electrodes and cells to provide information about the degradation of nickel electrodes as a function of cycling. We hope that it will eventually be possible to make reliable predictions of cycle life based on impedance measurements.

SUMMARY

Impedances of fifteen electrodes from each of the four U.S. manufacturers were measured at 0.200 V vs the Hg/HgO reference electrode. This corresponds to a voltage of 1.145 for a Ni/H_2 cell. Measurements were also made of a representative sample of these at 0.400 V. At the higher voltage, the impedances were small and very similar, but at the lower voltage there were major differences between manufacturers. Electrodes from the same manufacturer showed only

small differences. The impedances of electrodes from two manufacturers were considerably different in 26% KOH from those in 31% KOH. These preliminary results seem to correlate with the limited data from earlier life testing of cells from these manufacturers. We are following the impedances of cells being tested for Space Station Freedom and are doing more impedance measurements of electrodes as functions of manufacturer, voltage, electrolyte concentration, and cycle history in the hopes of finding better correlations of impedance with life.

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TABLE I. - AVERAGE KINETIC RESISTANCES AND WARBURG SLOPES FOR THE ELECTRODES FROM THE FOUR DIFFERENT MANUFACTURERS AT 0.200 V vs. Hg/HgO

[Electrode area 42.9 cm^2.]

	Manufacturer							
	Hughes		Gates		Eagle-Picher		Yardney	
	KOH concentration, percent							
	26	31	26	31	26	31	26	31
R_{kin}, Ω	0.1	0.9	1.7	0.6	1.5	1.5	3.9	2.5
Warburg slope, Ω $sec^{-1/2}$	0.016	0.071	0.041	0.31	0.085	0.060	0.32	0.39

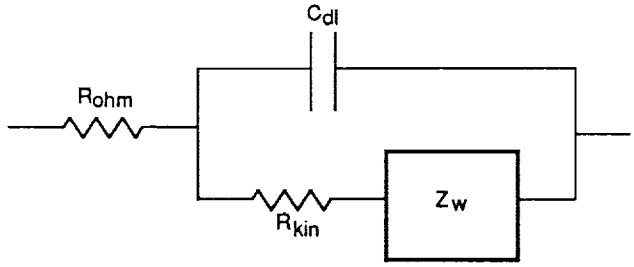

Figure 1. – Simplified circuit used for analysis of impedance data.

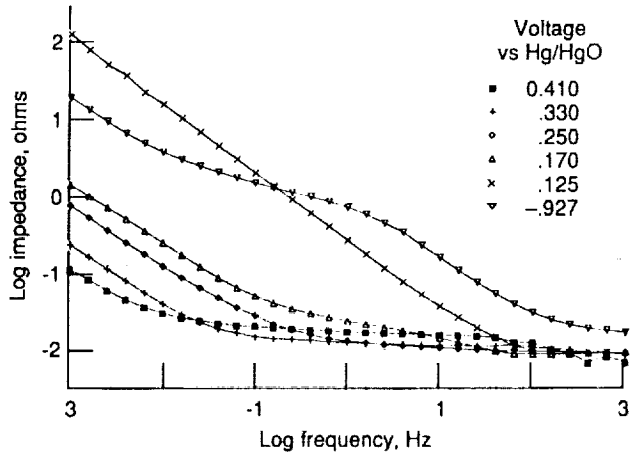

Figure 2. – Bode diagram, magnitude of impedance as function of voltage, Gates electrode, 42.9 cm^2.

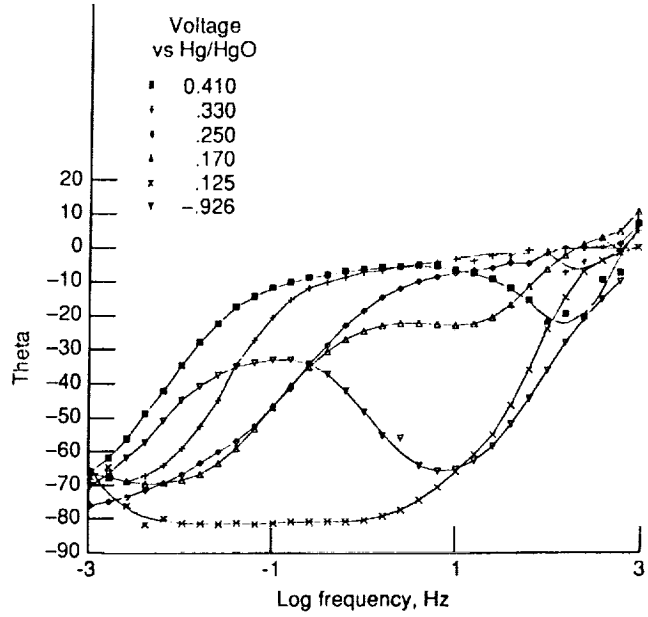

Figure 3. – Bode diagram, phase angle as function of voltage, Gates electrode, 42.9 cm^2.

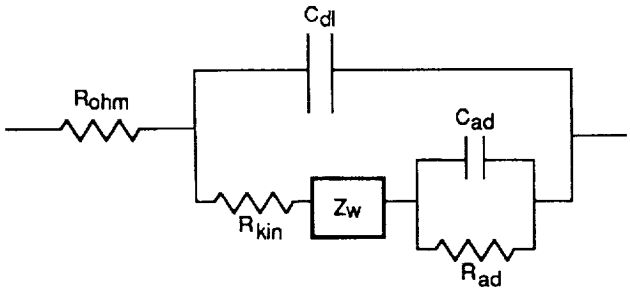

Figure 4. – Possible alternative circuit for more detailed analysis of impedance of nickel electrodes.

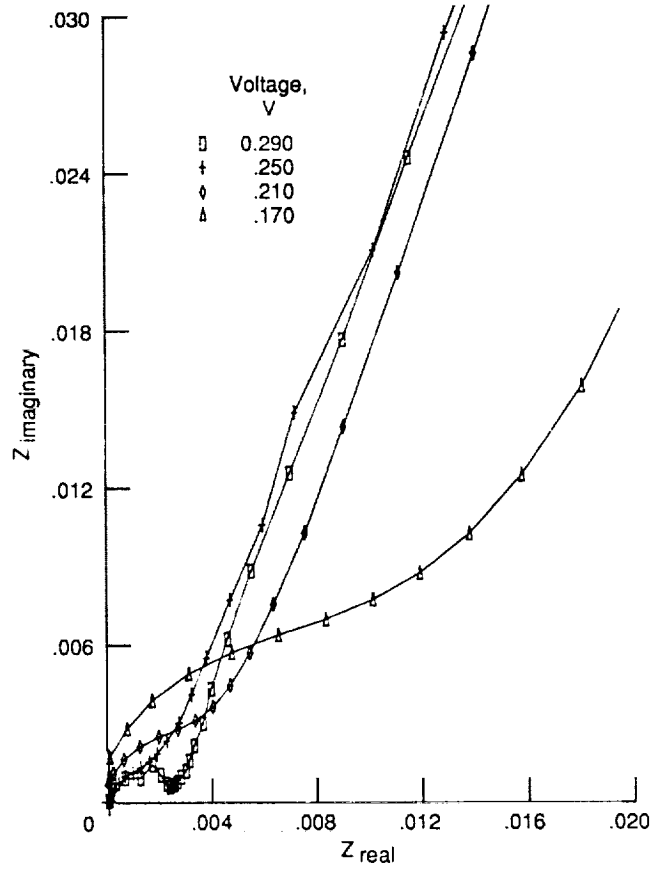

Figure 5. – Complex plane plot of some of the impedance data for the Gates electrode as functions of voltage in the range where the greatest changes take place.

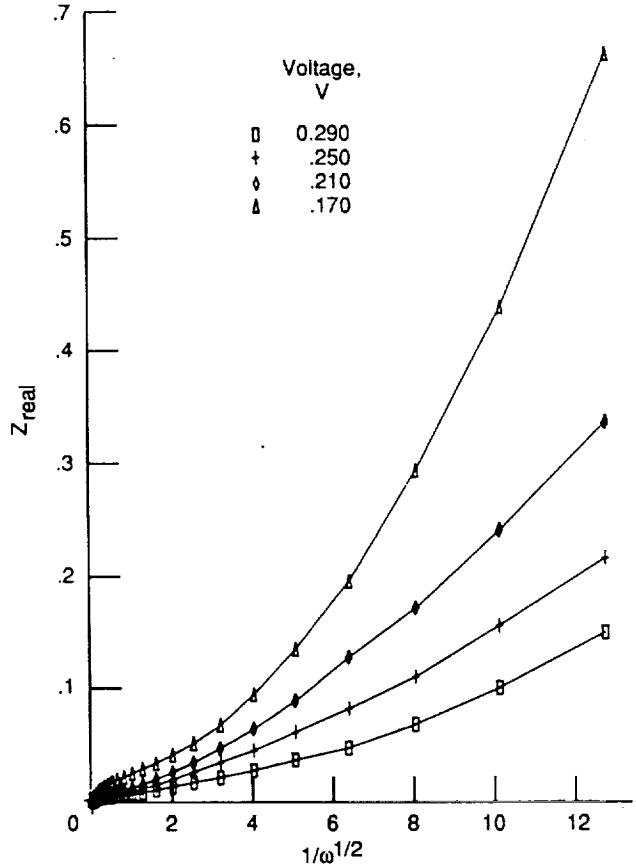

Figure 6. – Warburg plot of some of the impedance data for the Gates electrode as functions of voltage in the range where the greatest changes take place.

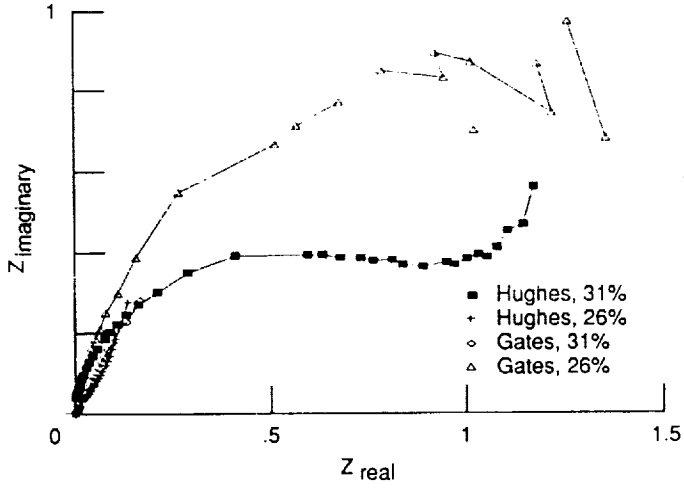

Figure 7. – Complex plane plot for impedance of electrodes at 0.200 V from two of the manufacturers in 31 and 26% KOH.

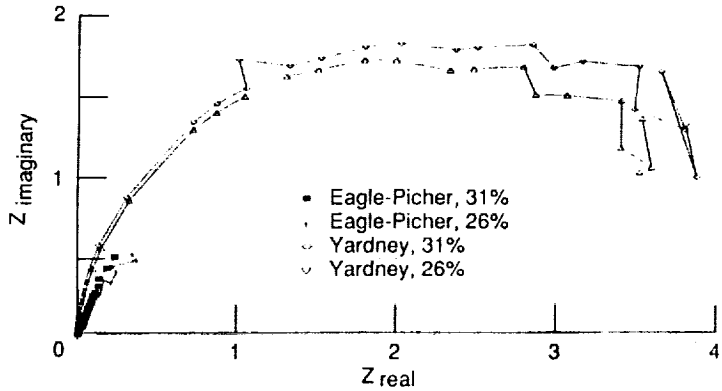

Figure 8. – Complex plane plot for impedance of electrodes at 0.200 V from the remaining manufacturers in 31 and 26% KOH. Note difference in scale from prior plot.

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16. Abstract

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