

## Impedances of nickel electrodes cycled in various KOH concentrations

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### **Abstract**

Recent work has shown that Ni–H<sub>2</sub> cells cycled in 26% KOH have much longer lives than those cycled in other concentrations. As part of an ongoing program to try to correlate the impedances of nickel electrodes with their life and performance, impedances were measured of a number of electrodes from these tests that had been cycled in concentrations from 21 to 36% KOH. These had been cycled under double-time LEO conditions at 80% DOD to failure. Cell life ranged from about 1000 to 40 000 cycles. After cycling ten times to reduce possible changes due to storage, impedances were measured at five voltages corresponding to low states of charge. The results were analyzed using a standard circuit model including a Warburg impedance term. Lower kinetic resistances and Warburg slopes were found for several electrodes which had been cycled in 26% KOH even though they had been cycled for a much longer time than the others. Interpretation of the data is complicated by the fact that the cycle lives, storage times and failure mechanisms varied. Several other circuit models have also been examined, but the best correlations with life were found with parameters obtained from the simple model.

### **Introduction**

The effects of electrolyte concentration on the life of Ni–H<sub>2</sub> cells have recently been studied [1, 2]. Cycle lives of up to 40 000 cycles were achieved with 21% KOH. Since no impedances have ever been measured on electrodes that had been cycled for such long times, these electrodes were investigated to determine the relationship of impedance to KOH concentration and cycle life. Impedances of Ni electrodes have been studied by many investigators [3–7]. It has been found that impedances increase by several orders of magnitude as the electrode goes from the fully charged to the fully discharged state. Results from different investigators are similar qualitatively but not quantitatively. Our earlier studies have shown this is not due to lack of reproducibility of the impedance measurements but is due to differences in preparation and storage of the electrodes. Cells from a given lot from each manufacturer have been shown to have impedances that are very similar [7] provided that they have been cycled and stored in the same way, but cells from different manufacturers [8] and electrodes that have been stored for relatively long periods of time [3] have different impedance characteristics. Thus impedance measurements provide a promising method for study of

nickel electrodes from different sources and under different operating conditions, especially since many other methods of study, i.e. X-rays, do not show clear distinctions between electrodes. However, considerable care must be taken in *comparing* electrodes and cells from different sources to insure that the cycling and storage conditions are the same. An additional advantage of impedance measurements is that they are electrical in nature; hence they show promise of being able to provide information for constructing cell models which would be able to be used in predicting charge and discharge curves and other electrical characteristics. These models would ideally incorporate differences due to cell manufacturer, KOH concentration, cycle regime and numbers of cycles. Such models are not available as yet, but are needed by system designers to predict the behavior of cells and electrodes under various pulse and steady-state loads.

## Experimental

The electrodes examined in this study were provided by Hughes Aircraft Corporation from their study on the effects on life of various KOH concentrations [1, 2]. The cells were boilerplate cells with six electrodes each and were cycled in a double-time LEO regime at 80% DOD. All electrodes were from the same lot. Each cell had six electrodes, of which the top and bottom electrodes were used in this study. The results of the cycling experiments are summarized in Table 1. One uncycled electrode from the same lot was also studied.

Measurements were made using a Solartron 1250 frequency response analyzer and a Solartron 1286 electrochemical interface from 1000 to 0.001 Hz (six decades). At high frequencies a 1 mV RMS signal was used in order to keep the current within the limitations of the instruments. Some measurements at the lower frequencies where the impedances were much larger

TABLE 1

Life test results of Ni-H<sub>2</sub> cells at 80% depth-of-discharge

Cell no.	[KOH] (%)	No. cycles to 0.9 V	No. cycles to 0.5 V	Total no. cycles	Failure mode
BP1	21	5047	> 38191	38191	soft short
BP2	26	39230	> 39573	39573	soft short
BP3	26	4329	9241	9241	low EODV
BP4	31	2979	3275	3286	low EODV
BP5	31	3620	4230	4230	low EODV
BP6	36	1268	1845	1845	low EODV
BP7*	21	1037	6508	9402	low EODV
BP8	26	> 30549	> 30549	30549	removed
BP9	26	23598	> 24594	24594	soft short
BP10	23.5	4803	28495	28495	soft short

\*Cycled at 70% depth-of-discharge (DOD) from 1644 to 4644 cycles and after 6508 cycles.

were made using a 5 mV signal to improve the sensitivity of the measurements. Data were taken using ZPLOT software (Scribner Associates, Charlottesville, VA).

A Hg/HgO reference electrode was used. For comparison with voltages in actual cells, Table 2 lists the voltages used along with the same voltages with respect to that of a H<sub>2</sub> electrode at the pressure that would be found in a sealed cell [3].

The electrodes studied here had been removed from the boilerplate cells after failure, rinsed and dried, and stored until the complete set of cells had failed. It is known that storage affects the impedance [3], but the magnitude of the effect and the effects of dry versus wet storage are unknown. In order to bring the electrodes as much as possible to a consistent state, they were cycled ten times, starting with four cycles at a C/10 charge rate for 18 h and a C/4 discharge rate to a cut-off voltage of -0.50 V. The next five cycles were at a C/4 charge rate with 10% overcharge and a C/2 discharge rate to 80% DOD. They were then charged again at a C/4 rate with 10% overcharge before taking the impedance measurements, starting with the highest voltages. Before measurements were taken, the electrodes were equilibrated at the desired voltage, usually until the d.c. current fell below 10 mA. The electrode that had not been used in the cycling tests was conditioned in the same way.

The top and bottom electrodes from each cell were studied. In general the impedances from the top electrodes were somewhat higher. When the cells had been dismantled, it was noted that the top electrodes were drier [1]. The lesser amount of electrolyte during cycling is probably the cause of the higher impedance. The differences were generally much smaller than those between cells, so the parameters from the two electrodes were averaged for subsequent analysis.

The choice of potentials for the cell measurements was made based on the results of earlier measurements with electrodes from different manufacturers [8, 9]. It has been found that at high states of charge the impedances are low, and differences between manufacturers are also small. However at low states of charge (in the voltage range from about 0.330–0.170 V versus Hg/HgO electrode or from 1.275–1.115 V in a cell) they increase by several orders of magnitude, and there are significant differences between manu-

TABLE 2

Voltages of Ni-H<sub>2</sub> cells corresponding to various half-cell voltages

Ni vs. Hg/HgO	Comparable Ni-H <sub>2</sub>
0.170	1.115
0.200	1.145
0.255	1.200
0.290	1.235
0.330	1.275

facturers. At voltages below 0.170 V the impedances are still higher, but there are smaller differences between electrodes from different manufacturers. There is also much more scatter, and a much longer time is required to reach equilibrium, so that the voltage range from 0.330–0.170 seems to be the best range for comparison.

## Results and discussion

Bode plots and complex plane plots for one of these electrodes are shown in Fig. 1. Figure 1(c) shows the overall complex plane curves, while Fig. 1(d) shows the expanded portions at the higher frequency range. These figures are for an electrode cycled in 26% KOH for 30 549 cycles, at which point the cell was removed for further analysis. The same trends were observed for all the electrodes as the voltage was changed.

The simplest equivalent circuit that can be postulated for a battery electrode is shown in Fig. 2(a) where  $Z_w$  represents a Warburg impedance

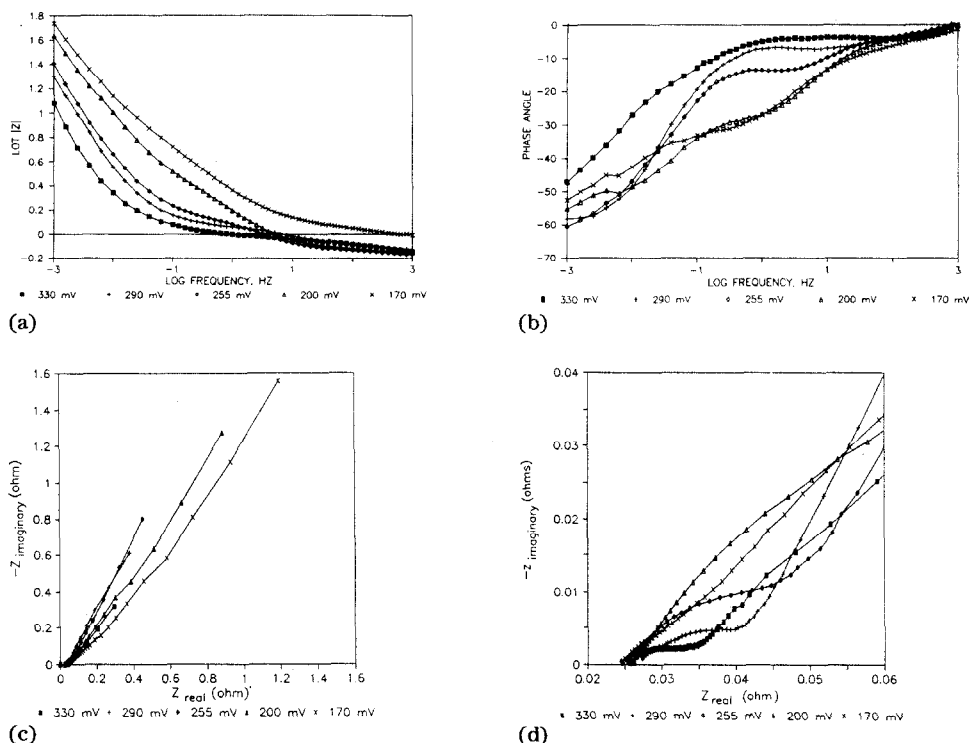


Fig. 1. Changes of impedance with voltage for electrode cycled 30 549 cycles in 26% KOH. (a) Bode magnitude plot, normalized data. (b) Bode theta plot. (c) Complex plane plot. (d) Expanded high frequency portion of complex plane plot. (c) and (d) are non-normalized data. Electrode area = 27.9 cm<sup>2</sup>.

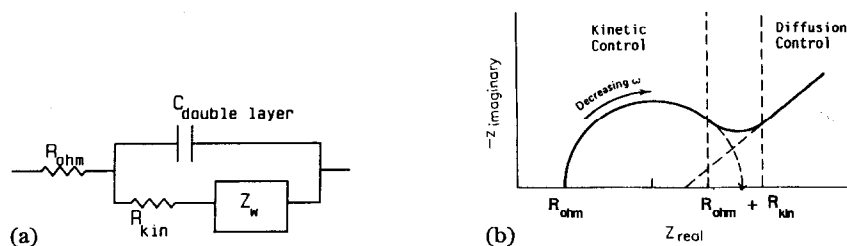


Fig. 2. (a) Simple circuit used for initial analysis of impedance data. (b) Complex plane plot for typical circuit of (a).

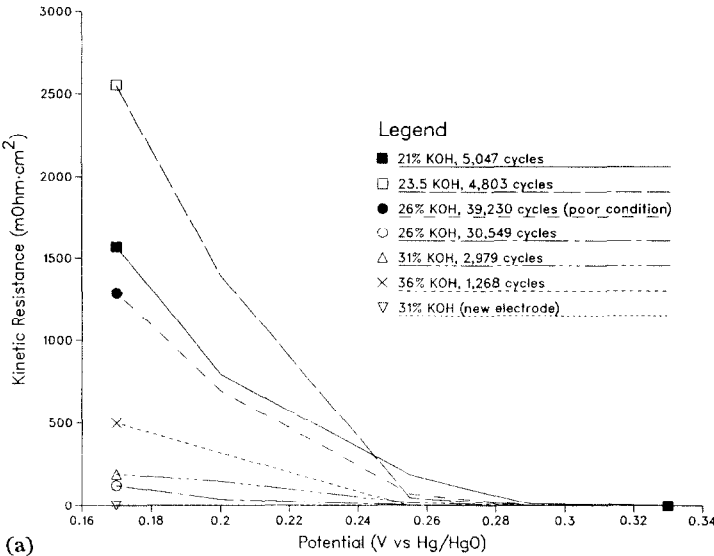
due to slow diffusion processes. The complex plane plot for such a circuit is given in Fig. 2(b), where the ohmic resistance is the intercept of the curve with the  $X$  axis, and the kinetic resistance is the diameter of the semicircle. Other parameters that can be obtained by further analysis are the Warburg slope and the capacitance. For a planar electrode the Warburg slope is proportional to  $1/CD^{1/2}$  where  $C$  is the concentration of diffusing species and  $D$  is the diffusion coefficient. This model is satisfactory for simple reactions on planar electrodes but is not adequate for more complicated reactions and for porous or rough electrodes. Several models have been proposed for porous electrodes [10, 11], and modeling studies are being carried out for electrodes such as the nickel oxide electrode where the metallic substrate is covered with relatively thick layers of oxides of mixed valences and conductivities [5, 12]. Until the models for these electrodes are developed further, we will use some simple equivalent circuits as approximations, first looking at the circuit of Fig. 2(a).

The high frequency portion of the experimental curves in the complex plane representation often cannot be fit very satisfactorily by a semicircle, especially at higher voltages as can be seen in Fig. 1(d). In such cases we have graphically fit the best semicircle to the initial part of the curve. The Warburg slope is interpreted here as an empirical parameter related qualitatively rather than quantitatively to the diffusion resistance where a higher slope signifies a slower rate of diffusion and a low slope a more rapid rate of diffusion. The capacitance values were also obtained from the original 'ZPLOT' figures by drawing the best semicircles. Plots of the kinetic resistances, Warburg slopes and capacitances for the electrodes are given in Fig. 3 which illustrate that with the exception of the uncycled electrode, the impedances at the lower voltages are smallest for the electrodes cycled in 26% KOH which lasted for 30 549 cycles. The high values for the other electrodes cycled in 26% KOH are believed to be due to their poor condition and that they probably failed by soft shorts. These Figures also illustrate the large changes in impedance parameters with voltage. With few exceptions the parameters vary regularly as the voltage is changed.

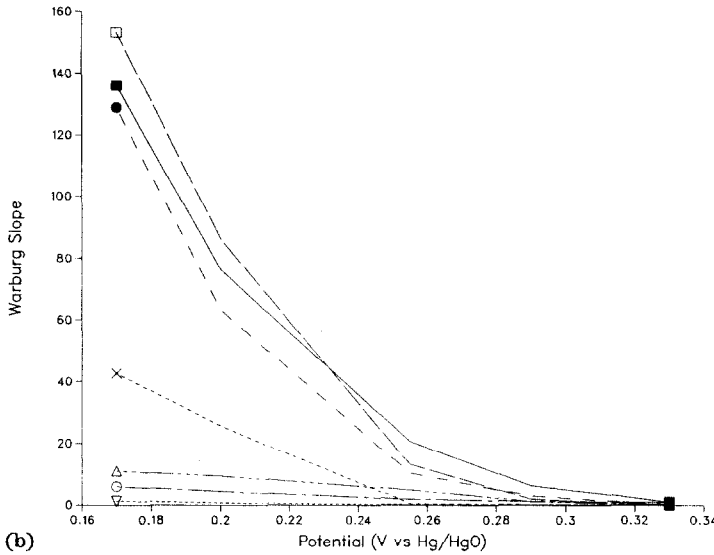
All but three of the electrodes in this study had been cycled to failure (the electrodes from the cell which had been cycled over 30 000 cycles in 26% KOH before the cell was removed and the uncycled electrode). The

fact that the impedances are different indicates that the impedance parameters are probably not an indication of failure, otherwise they would all be similar.

Intuitively, one would expect that impedances would increase as the number of cycles increases and the cell approaches failure. However, this does not appear to be the case here. The effects of the KOH concentration seem to be more important than the numbers of cycles. We have very little



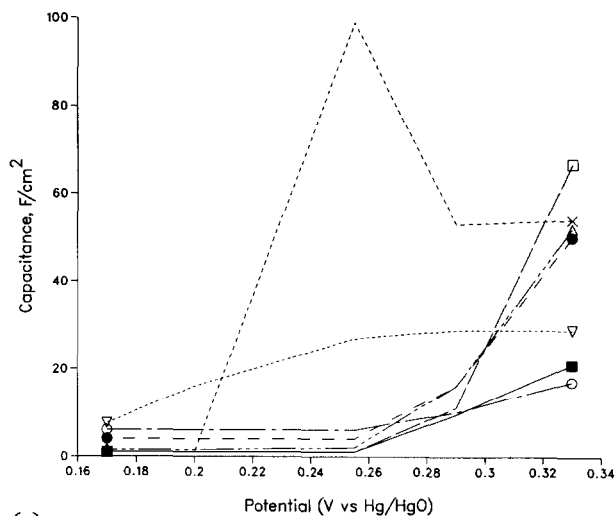
(a)



(b)

Fig. 3.

(continued)



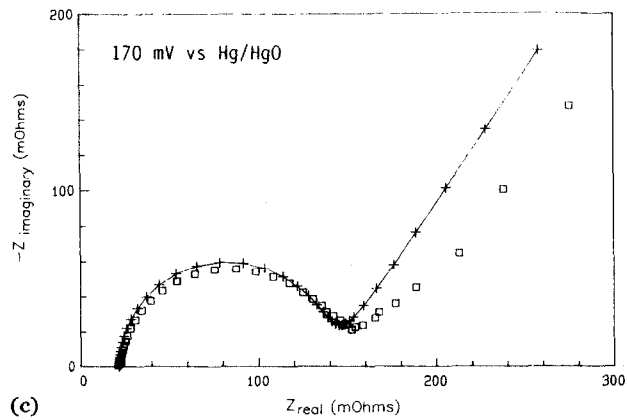
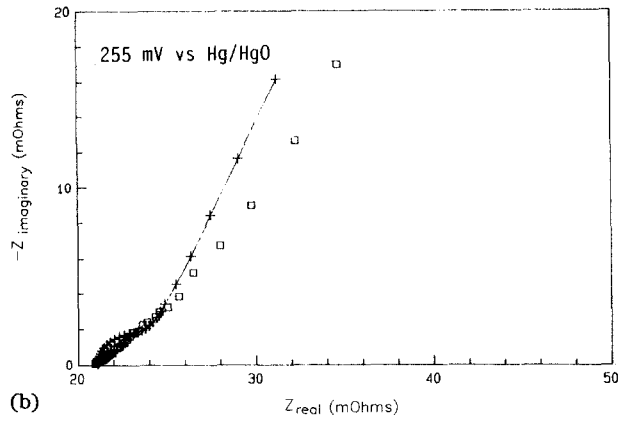
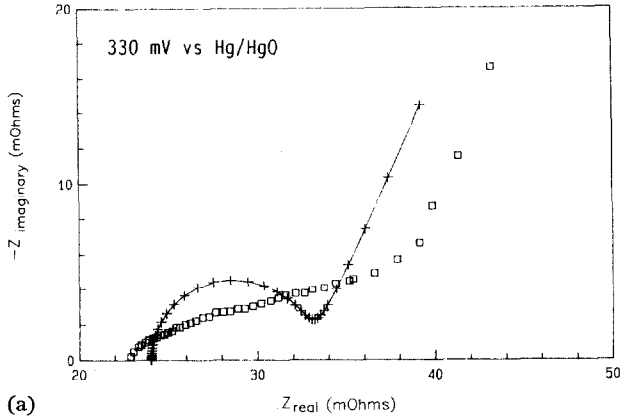
(c)

Fig. 3. Impedance parameters for various electrodes obtained from graphical analysis using circuit of Fig. 2. All parameters are normalized. (a) Kinetic resistances, (b) Warburg slopes, (c) capacitances.

other information about impedance as a function of cycle history. Two Ni-Cd cells that have been cycled for 6500 cycles showed *decreases* in impedance with cycling up to 1500 cycles and then stayed fairly constant [13]. However, these cells had been stored for about five years before the measurements were taken, so the effects of storage cannot be separated from the effects of cycling. We have taken measurements on about 18 'flightweight' Ni-H<sub>2</sub> cells (Inconel casings) being tested for NASA missions after acceptance and after about 500–800 LEO cycles. It has not been possible to interrupt the cycle test and take further measurements to any extent since then; however, a few measurements indicate that the impedance is *increasing* somewhat after about 5000 cycles.

Although some of the cells failed by soft shorts and others by loss of capacity (Table 1), this is not thought to be a major factor. The fact that a *cell* failed by a soft short does not mean that *each* electrode in the cell failed in this way, only that at least one electrode of the cell had a soft short. From observations of the physical condition of the electrodes that we tested, we believe that only the ones that had been cycled for 39 000 cycles had soft shorts, those indicated on Fig. 3 as being in poor condition. We feel that if these electrodes and the uncycled electrode are excluded, the conclusion that lower impedance is related to longer life and to the KOH concentration is probably valid.

The capacitances obtained from this analysis are very large at the higher voltages and probably reflect not only the double layer capacitances but diffusion factors and any adsorption capacitances. They are obtained from plots of  $Y'/w$  versus  $Y''/w$  where  $Y'$  and  $Y''$  are the real and imaginary parts



**Fig. 4.** Comparison of some experimental and simulated complex plane plots using best parameters obtained using EQUIVALENT CIRCUIT program and circuit of Fig. 2(a). Uncycled electrode:  $\square$ , experimental;  $+$ , simulated.



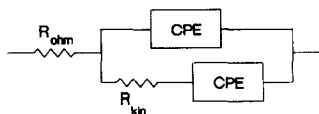


Fig. 5. Circuit with two constant phase elements used for further analysis of data.

of the complex admittance, i.e. the inverse of the complex impedance. (In a circuit with only one parallel RC circuit and no diffusion elements, the double layer capacitance is obtained unambiguously from this procedure). If other circuit elements are present, one can consider the capacitance obtained by this method as an 'effective capacitance' rather than a true double layer capacitance. As will be seen below, the use of other more detailed circuit models gives similar values for ohmic resistances and kinetic resistances, but the capacitances vary greatly depending on the model.

It is obvious from examination of the curves that a more complicated circuit is needed, particularly at higher voltages. Several circuits have been examined using commercially available programs which use a non-linear least-squares procedure to fit the data (ZFIT-CNRS from Schlumberger Instruments and EQUIVALENT CIRCUIT from Princeton Applied Research). Preliminary estimates of the parameters are required as inputs to these fitting programs, which were obtained in part from the graphical analysis of the data. In an attempt to reduce the subjectivity of the initial analysis of the simple circuit of Fig. 2(a), the EQUIVALENT CIRCUIT program was used to find the parameters rather than obtaining them from the graphs as before. The experimental and calculated curves are shown in Fig. 4 for three voltages for the uncycled electrode. The calculated curves do not fit the experimental curves well, and the parameters derived from the computer analysis do not show as consistent trends with voltage as did those obtained graphically.

Two other equivalent circuits have been extensively studied [14], and several others have been tried. The circuit in Fig. 5 incorporates two constant phase elements (CPE). These have been suggested for modeling fractal electrodes and for certain cases of diffusion, but the interpretation of this element is still not clearly understood. The calculated curves agree better with the experimental curves as shown in Fig. 6. Many of the parameters, as with the former analysis, do not show a regular trend with voltage. However, the capacitance associated with the CPE element which is in series with the kinetic resistance does increase regularly with voltage and may prove to be a suitable parameter for comparison.

Another equivalent circuit is suggested by examination of the curves in the Bode phase angle plot in Fig. 1(b). The plateau in the data at 255 mV suggests that a circuit with more than one RC circuit might be a better fit to the experimental curves. Figure 7 gives the circuit used. Again, we can fit the experimental curves more closely (Fig. 8), but the parameters still do not always vary regularly with voltage. Table 3 gives the results of this analysis for the uncycled electrode. Similar results were obtained for the

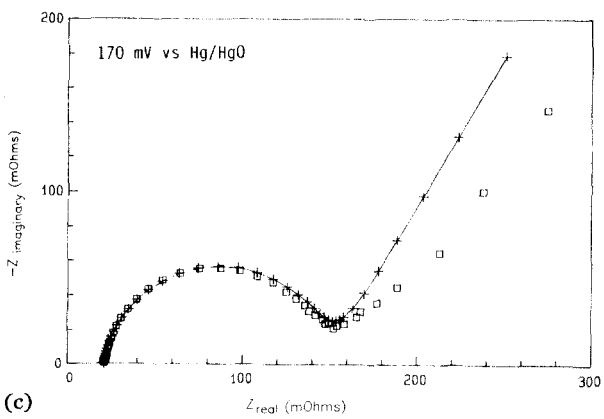
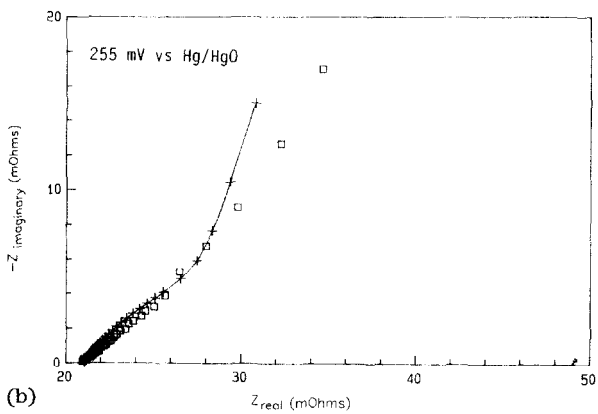
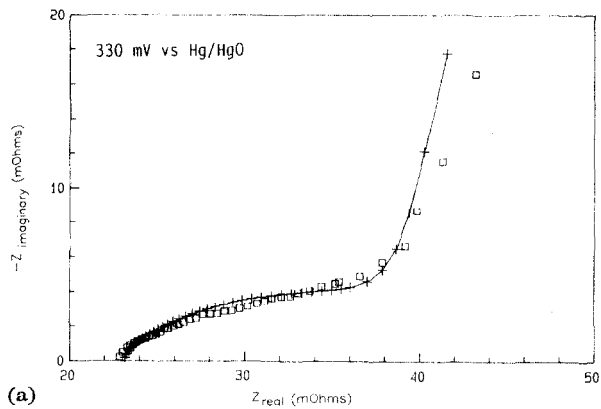


Fig. 6. Same as Fig. 4 using circuit of Fig. 5.

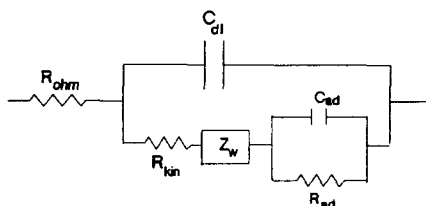


Fig. 7. Circuit incorporating adsorption capacitance and resistance for further analysis of data.

other electrodes. The best parameters for comparison with cycle life so far seem to be the Warburg slopes at the lower voltages from the analysis of the simple circuit, since these can be determined accurately with a minimum of subjective judgement. The capacitance associated with the CPE element of the second circuit may also prove to be useful.

As mentioned above, the double layer capacitances obtained with these more detailed circuit models are much less than the 'effective capacitances' obtained with the simplistic model, often by several orders of magnitude, whereas the kinetic resistances obtained by the different models do not vary by more than a factor of two. The double layer capacitance values obtained with the more detailed model of Fig. 7 are of the same order of magnitude as those calculated using the BET surface area and are probably a good indication of the true double layer capacitance, since the adsorption and diffusion terms have been separated out. We feel that this latter model is a better physical approximation to the electrode, but because it consists of more elements, a least-squares computer fit requires extremely accurate data which are not always obtainable for these electrodes. One must remember that none of these equivalent circuit models can represent the true situation in the highly complex porous nickel oxide, but in the absence of an adequate theoretical model, a simple model is needed to obtain parameters for comparison of electrodes and cells.

The measurements here are intriguing, but obviously a much larger data base is needed to determine the effects of KOH concentration and cycle life on the impedance. We are planning to carry out experiments with individual electrodes to obtain a more complete set of impedance data as functions of manufacturer, KOH concentration, cycle life and storage conditions.

## Conclusions

Impedances were measured of electrodes from boiler-plate cells that had been cycled in KOH concentrations from 21–36%. These cells had been cycled under double-time LEO conditions at 80% DOD to failure. Cell life ranged from about 1000–40 000 cycles. Measurements were made at five voltages corresponding to low states of charge. The results were analyzed using a simple circuit model including a Warburg impedance term. With the exception of the uncycled electrode and the electrode that is believed to

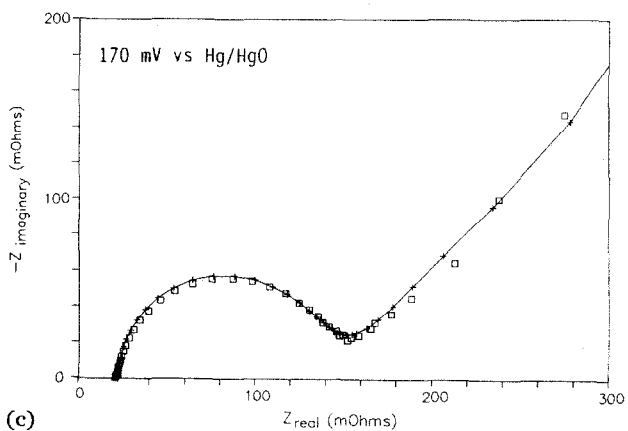
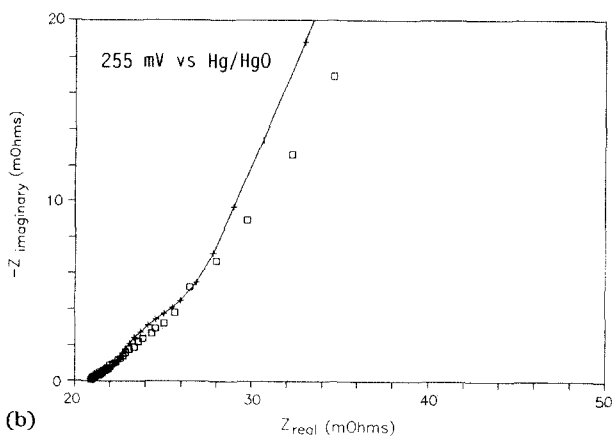
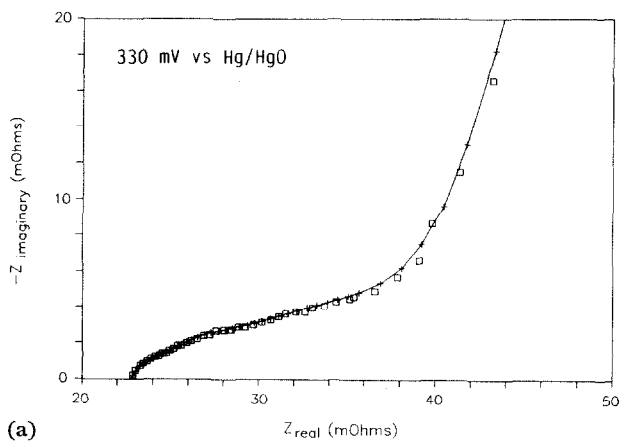


Fig. 8. Same as Fig. 4 but using ZFIT-CNLS program and circuit of Fig. 7.

TABLE 3

Impedance parameters at several voltages obtained by analysis with CNLS and ZFIT

	V vs. Hg/HgO				
	0.330	0.290	0.255	0.200	0.170
$R_{kin}$ ( $\Omega$ )	0.0052	0.00073	0.057	0.048	0.118
$C_{dl}$ (F)	1.19	3.65	0.48	0.43	0.5
$R_{adsorp}$ ( $\Omega$ )	0.0066	0.00087	0.0078	0.011	0.0097
$C_{adsorp}$ (F)	41	75	123	3.7	350
$R_{diff}$ ( $\Omega$ )	0.17	0.15	0.56	0.59	1.00
$T$	479	436	420	443	477
Phi	0.70	0.67	0.65	0.63	0.61

have failed by a soft short, the kinetic resistances and Warburg slopes were greater for those electrodes which had failed earlier after cycling in KOH concentrations other than 26% and smallest for the electrode that had been cycled for over 30 000 cycles in 26% KOH. The impedances are not an indication of failure since the electrodes had different impedances although they had all been cycled to failure. The results are not conclusive, since in addition to the varying numbers of cycles that the electrodes had been subjected to, the cells had been stored after failure for varying lengths of time, which is known to affect the impedance. In order to minimize the effects of storage, the electrodes were cycled 10 times before the impedance measurements were taken.

Several more detailed circuit models were also tried. The data can be fit more satisfactorily with these, but the parameters obtained have greater scatter and do not correlate as well with the cycle lives as those obtained from the simple circuit. To improve the data base we are initiating a comprehensive study of the effects on the impedance of electrodes as functions of storage conditions, cycle life, KOH concentration and manufacturer.

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