DOE/NASA/12726-13
NASA TM-82702

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(NASA-TM-82702) PREPARATION AND CHARACTERIZATION OF ELECTRODES FOR THE NASA REDOX STORAGE SYSTEM (NASA) 17 p HC A02/MF A01 N81-30522
CSCL 10C
Unclas
G3/44 27214

Margaret A. Reid, Randall F. Gahn,
Jerri S. Ling, and JoAnn Charleston
National Aeronautics and Space Administration
Lewis Research Center

Work performed for
**U.S. DEPARTMENT OF ENERGY**
**Conservation and Renewable Energy**
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Prepared for
Electrochemical Society Meeting
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National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

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Washington, D.C. 20545
Under Interagency Agreement DE-AI04-80AL12726

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# PREPARATION AND CHARACTERIZATION OF ELECTRODES FOR THE NASA REDOX STORAGE SYSTEM

by Margaret A. Reid, Randall F. Gann, Jerri S. Ling,
and JoAnn Charleston

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

E-739

## SUMMARY

The current status of electrodes for the NASA Redox energy storage system based on iron and chromium chloride reactants is discussed. Difficulties in making well-behaved electrodes for the chromium side of the flow cell have been largely overcome. The physical properties of several lots of felt were determined. Refined procedures were developed for evaluating electrode performance in lab-scale cells.

Experimental procedures for evaluating electrodes by cyclic voltammetry are described which minimize the IR losses due to the high internal resistance in the felt (distributed resistance). Improved methods for preparing electrodes were discovered which reduced the coevolution of hydrogen at the chromium electrode and eliminated the drop in voltage on discharge occasionally seen with previous electrodes. Single cells of 0.33 $ft^2$ area with improved membranes and electrodes are operating at over 80 percent voltage efficiency and coulombic efficiencies of over 98 percent at current densities of 16 to 20 $amp/ft^2$.

## INTRODUCTION

In the NASA-Redox energy storage system, a solution of oxidizing agent, ferric chloride in HCl, is pumped through one compartment of an electrochemical cell, and a solution of a reducing agent, chromous chloride in HCl, is pumped through the other compartment. An anion-exchange membrane separates the compartments and prevents the cross-mixing of the reactive cations. Electrodes consist of carbon felt, catalyzed on the chromium side by trace quantities of Au and Pb (10 to 200 $\mu g/cm^2$). No catalyst is needed on the iron side. A schematic diagram of a single Redox cell and the electrode reactions is shown in figure 1. During discharge chloride ions move from the cathode compartment to the anode compartment, and hydrogen ions move in the opposite direction. On charge all reactions are reversed. This system has been under development at Lewis Research Center (LeRC) since 1974 with funding from NASA and DOE. Since all species are fully soluble, there are no life-limiting factors such as shape changes, inactive forms of reactants, and dendrite formation. There are also many advantages in system sizing and control that have been discussed elsewhere (refs. 1 and 2).

Semi-permeable membranes have been developed over the past 6 years that are sufficiently conductive and selective for use for photovoltaic and wind energy storage applications. Methods of keeping the system in balance have been developed. Flow characterization and analysis of shunt currents have been carried out, and hardware has been scaled up with little difficulty (refs. 3 and 4).

Development of the electrodes has been carried out in conjunction with the above studies. The rates of oxidation and reduction in the ferrous and ferric ions are rapid enough that uncatalyzed carbon felt can be used on the iron side of the cell, but a catalyst is needed on the chromium side since the rate of reduction of Cr(III) to Cr(II) is slow on most surfaces. The catalyst must also have a high overvoltage for hydrogen since thermodynamically hydrogen is evolved before chromium is reduced. Appreciable coevolution of hydrogen reduces the coulombic efficiency and also over the course of many cycles allows the system to get out of balance electrochemically and thus lose effective capacity. Giner, Inc. of Waltham, MA (ref. 5) found under contract that trace amounts of Au and Pb (12 to 25 μg Au/cm$^2$ and 100 to 200 μg Pb/cm$^2$) deposited on the felt would meet the requirements for an effective catalyst. Lead metal has long been known as an effective catalyst for the reduction of $Cr^{+3}$ to $Cr^{+2}$. The presence of trace amounts of Au seems to be necessary to produce a surface on which the Pb plates (or adsorbs) uniformly during the charging cycle. The Au-Pb catalyst also improves the discharge rate of the cell.

In scaling up the NASA-Redox system for photovoltaic energy storage, a 1-kW preprototype system has been built at NASA Lewis Research Center and is now being integrated and tested with the NASA/DOE Photovoltaic Systems Test Facility. To construct this system, a new lot of carbon felt was purchased from the vendor, Fiber Materials, Inc. of Biddeford, ME. This is produced by thermal decomposition of 1/8-inch rayon felt. Final thickness as measured by a standard thickness gauge is from 0.060 to 0.110 inch with most samples in the range 0.080 to 0.090 inch. When used in the flow cell stacks, it is slighty compressed by 0.012 to 0.016 inch. It was found that electrodes prepared with this new lot had much higher rates of hydrogen evolution than those made with the original lot as well as displaying a lower voltage in the latter stages of discharge (fig. 2). Discussions with the manufacturer did not reveal any obvious reason for this behavior. A study was initiated to discover the reasons for the poor electrode behavior and to determine ways to prepare satisfactory electrodes from different lots of felt.

## EXPERIMENTAL

Preliminary characterization. - X-ray characterization of different lots of felt showed no differences in the degree of crystallinity, so that the differences were assumed to be due to surface effects. Gross differences in the rates of oxidation in air at 450° to 500° C were observed. Cleaning in inorganic acids reduced the rates of oxidation considerably. Whether this was due to the removal of trace inorganic impurities or to modification of the carbon surface has not been determined.

Differences in wettability were observed at NASA Lewis Research Center and quantified by Giner, Inc. (ref. 6). These differences in wettability apparently led to differences in the amount of gold deposited on the felt, either adsorbed or reduced by reactive sites. Neutron activation analysis and x-ray fluorescence analyses confirmed this. However, even when procedures were modified so that the same amount of gold was deposited on the surfaces of different samples, there were still differences in the electrochemical behavior in both lab cells and in cyclic voltammetry experiments.

Materials and apparatus. - All chemicals used were C.P. Deionized water was used for preparing all solutions.

The laboratory subscale flow cell for evaluating experimental electrodes has been described in previous publications (refs. 1 and 2) and was equipped with a rebalance cell (ref. 2) to recombine any evolved hydrogen with excess ferric ion produced as a net result of side reactions. The amount of hydrogen evolved as a function of state of charge of the cell served to characterize the individual electrodes. Most lab scale experiments were carried out in cells with 1-1/2 by 1-1/2-inch electrodes (14.5 $cm^2$) using 40 $cm^3$ of each solution. This corresponds to 1.075 amp-hour of capacity with the 1 M solutions used. An amp-hour meter on the working cell allows determination of the coulombic efficiency for each cycle.

Hydrogen evolved from the chromium side of the working cell was fed to the hydrogen electrode of the rebalance cell. A second meter on the rebalance cell measured the amp-hours produced by the hydrogen as it reacted with excess $Fe^{+3}$ in this cell. Thus the proportion of current going to produce the byproduct hydrogen could be monitored continuously.

All cyclic voltammetry experiments described here were carried out by scanning at a rate of 10 mV/sec from 0.00 to -1.00 volt with respect to the Ag/AgCl electrode with the exception of the comparison scan of the $Fe^{+3}/Fe^{+2}$ curve from 0.00 to 1.00 volt. Active electrode area was 2 $cm^2$ (1.20 x 1.67 cm). Strips of the felt to be examined were cut the appropriate size (1.20 2.67 cm) and placed in the sample holder. The sample holder is a standard small binder clamp about 3/4 inch wide obtainable in office supply stores. Copper strips are soldered to the insides of the jaws and a threaded rod 1/8 inch in diameter is soldered to the top. The active area was held tightly in the waxing shield so that hot wax would not penetrate into it, and the upper portion including the electrode holder was dipped into hot wax.

The waxing shield is made from a steel strip about 30 mils thick, 1 inch wide, and 4-1/2 inches long with blunt ends so that the felt is not cut when the shield is tightened. The strip is bent in half as shown and holes drilled for a bolt to tighten the jaws on the felt. The jaws are tightened enough so that the wax does not wick up into the active portion but not so tightly that the felt is cut (about 0.5 mm).

The wax bath used was a pattern wax with a m.p. of 150° to 175° C. Best results were obtained when the bath was held at 130°±5° C. This procedure ensured that the solution would contact only the desired portion of the felt as well as provide good electrical contact between the felt and holder. See figure 3 for details of the electrode preparation and arrangement of electrodes in the cell. The cell was a 150 ml beaker with a Teflon top machined to fit. Holes were drilled in this for electrodes. A Ag/AgCl reference electrode was used. Counter electrodes were carbon rods contained in fitted glass tubes. All solutions were 2 M with respect to HCl as in most of the flow cell measurements. When measurements were taken in $CrCl_3$ solutions, the Cr(III) concentration was 0.05 M rather than the 1.00 M presently used in cells. The use of these concentarations and scan rates allowed sufficient separation of the $Cr^{+3}$ reduction peak and the rise in current due to hydrogen evolution. About 80 to 85 ml of solution were used. Most scans are depicted after 4 to 5 sweeps when the curves became reasonably steady. Many experiments were run for much longer times, and significant changes were noted in some cases as described below. No attempt was made to correct for IR drop between the reference and working electrodes since the purpose was only to make comparisons between electrodes although approximation of the rate constant can be made. These points will be discussed later along with the consequences of changing the electrode size, shape, and mounting.

## RESULTS AND DISCUSSION

Subscale flow cell studies. - Some of the results of the hydrogen evolution studies in subscale flow cells are shown in figure 4. The amp-hours measured on the rebalance cell are plotted against the open-circuit voltage indicating the amoaunt of hydrogen evolution as a function of state of charge of the system. The state of charge is related to the open-circuit voltage using the Nernst equation

$$E_{OCV} = 1.075 - 0.059 \log[Fe^{+2}][Cr^{+3}]/[Fe^{+3}][Cr^{+2}]$$

These data are for the first charging cycle, since when a cell gets out of balance due to $H_2$ evolution, the ratio of $[Cr^{+3}]/[Cr^{+2}]$ no longer equals the ratio of $[Fe^{+2}]/[Fe^{+3}]$, and the same open-circuit voltage corresponds to a different state of charge for the system. If we compare curve A (our original felt) with curve B (the new lot of felt) we see that with the original felt very little hydrogen was evolved until the system was about 90 percent charged compared to about 75 percent state of charge with the newer felts. Both of these were cleaned in $H_2So_4$.

Since the preliminary examination indicated that the differences between the felts was a surface effect, these results could be due to organic impurities, inorganic impurities, differences in functional groups on the surface, or a combination of the above affecting the deposition of the catalyst. Many other electrode cleaning procedures were tried including cleaning in $HNO_3$, concentrated HCl, and no cleaning. Other pretreatments include heating in air at 800° F and in $H_2$ at 1600° F. Plating methods included plating gold in situ followed by addition of lead to the chromium solution, plating of both Pb and Au at the same time in situ, and deposition of gold by thermal decomposition of $AuCl_3$. The latter method gave the most consistent results, and all data in figure 4 are for this procedure. It can be seen that superior results were obtained by cleaning the felt in $HNO_3$ (curve E). Since this figure was prepared, newer lots of felt have shown performance intermediate between the "new" and "old" felts.

The best results to date have been obtained by using an improved pretreatment process combined with an improved method of deposition of the gold. Data for the newer electrodes is given in figure 5. In this figure, as in figure 4, the data presented are for the first cycle since the open-circuit voltage cannot be correlated readily with the state of charge if the cell is out of balance. Improved performance is obtained in subsequent cycles. An important aspect of this method of preparation is that it produces well-behaved electrodes from most lots of felt tried so far, so that characterization of the felt is no longer a major problem. With these electrodes, hydrogen evolution is negligible until high charging voltages are reached. High coulombic efficiencies (98.5 percent) can be obtained in small lab cells where the charging and discharging is carried out so that the current tapers as the charging or discharging process nears completion. (Charging of such cells is carried out at a constant current until a preset limiting voltage is reached, at which point the current tapers. Discharging is carried out at a constant load so that the current tapers as the open circuit voltage falls.)

Electrodes prepared in this manner exhibit similar characteristics when tested in the same manner in 1/3 $ft^2$ cells. When the current density during most of the cycle is between 16 and 20 ASF, coulombic efficiencies of over 98 percent and voltage efficiencies of over 80 percent are obtained. Figure 6(a) shows a typical charge-discharge curve of a 1/3-ft$^2$ cell with a low resistance membrane and "best" electrodes. Figure 6(b) shows the polarization curves at 30 percent DOD. Essentially all the polarization is due to the IR drop across the membrane.

Cyclic voltammetry screening tests. - Cyclic voltammetry has been found useful as a screening method when examining the behavior of different lots of felt and the effect of various treatments on the chromic oxidation and reduction and the hydrogen evolution. The electrode material is a porous felt composed of randomly oriented carbon fibers of about 25 μ diameter. Spacing between adjacent fibers varies at random but is probably less than 100 μ at most points. The usual equations for cyclic voltammetry are valid for smooth surfaces and cannot be rigorously applied here. We must rely here on comparison to electrodes known to behave well or poorly in cell tests.

In order to establish a baseline for cyclic voltammetry in this porous felt medium, experiments were first carried out with ferric chloride solutions. Curve A of figure 7 shows a sweep from 0.2 to 1.0 volt of 0.05 M $FeCl_3$ solution in 2 M HCl. As mentioned above, this is uncorrected for IR drop and was taken at a sweep rate of 10 mV/sec. The area under the curves corresponds to reduction on the cathodic sweep of essentially all the ferric ion contained in the pores of the felt and the subsequent oxidation of all of the resulting ferrous ion on the anodic sweep. The curves do not differ qualitatively from the usual cyclic voltammetry curves on planar electrodes. Thus the method appears to be useful for porous electrodes, even if it cannot be treated theoretically.

In all of the following curves, the voltage range is from 0.0 to -1.0 volt. Curve B shows the behavior of an uncatalyzed felt electrode in $CrCl_3$ solution showing very little chromium reduction.

Curves C through F show the effect of the various steps when preparing a catalyzed electrode by plating in situ. Curve C shows the behavior of uncatalyzed "good" felt in 2 M HCl. The hydrogen evolution current at -1.0 volt is about 2 mA and is much less than with most lots of felt. Curve D shows the effect on the hydrogen evolution current when 12.5 μg/cm$^2$ of Au is plated onto the electrode. The current at -1.0 volt is about 35 mA. In curve E we see the effect of adding saturated $PbCl_2$ solution to the solution (1 drop/10 cc solution, in this case amounting to 500 μg Pb/cm$^2$ of electrode area). The hydrogen evolution current at -1.0 volt has decreased to about 1 mA. In curve F, $CrCl_3$ has been added so that the chromium concentration is 0.05 M. We see here the characteristics of a well-behaved electrode, that is, high chromium current coupled with low hydrogen evolution current. Some electrodes prepared in various ways have shown higher chromium currents but only in conjunction with higher hydrogen currents. These electrodes did not perform well in lab cells. Thus, in relating the cyclic voltammetry to the performance expected in lab cells, it is more important to have a small hydrogen evolution current than an increase in chromium reduction activity once a reasonable chromium catalytic activity is obtained.

In curves G and H we see some typical results for electrodes prepared with Pb but without Au. (This particular electrode is highly oxidized and thus has high surface area and oxidized functional groups on the surface.) In curve G we see the behavior after 4 to 5 sweeps. The behavior appears acceptable, that is, high chromium current coupled with low hydrogen evolution current. However, after cycling for several hours (curve H), the hydrogen current has gone up and the anodic portion of the curve is separating into two peaks, the first probably corresponding to oxidation of $Cr^{+2}$ on a Pb surface and the second to oxidation of $Cr^{+2}$ on the carbon surface after most of the Pb has been removed from the surface or after $Cr^{+2}$ has been depleted in the vicinity of the Pb sites. Electrodes such as this in lab cells behaved well at first but with time showed the dip on the discharge curve as shown in figure 2. Many electrodes prepared with gold also showed this behavior. The assumption in this case is that the Au was not distributed well over the surface, local depletion of reactant occurs around the active sites, and a portion of the chromium oxidation takes place on carbon rather than Pb or Au.

Electrodes could be prepared satisfactorily for cyclic voltammetry experiments and in small lab cells by plating in situ, but it was found that in larger cells and stacks there was some reaction of the $AuCl_3$ with the membrane and some inhomogeneity in the gold distribution. It has been found most satisfactory to apply gold by thermal decomposition of AuCl at 260° to 280° C. Colloidal gold deposits were also investigated. Curve I shows the behavior of an electrode with 12.5 $\mu g/cm^2$ of colloidal Au deposited on the felt by formaldehyde reduction. This also showed high hydrogen evolution and was unsuitable for use in cells.

In curve J we see the cyclic voltammogram of an electrode prepared by $HNO_3$ cleaning of a lot of "bad" felt followed by thermal decomposition of 13 $\mu g/cm^2$ of Au onto the surface. This electrode proved satisfactory in lab cells but not in larger cells where the ratio of flow volume to surface area is smaller. Voltammograms of electrodes removed from cells and allowed to come into contact with air also have this general appearance. These cannot be reused without excessive hydrogen evolution.

In curve K we see the cyclic voltammogram of our best electrode so far, prepared with an improved pretreatment method and a modified gold deposition method. This was prepared from our "bad" felt which had previously been unusable. The hydrogen evolution is much smaller than that of the previous electrode. Cyclic voltammograms of these electrodes retain their shape after cycling for several days. In lab cells these electrodes do not develop a drop in the discharge curve with time.

At this point we conclude that if an electrode gives a cyclic voltammogram simiilar to that of curves F or K and retains this shape after repeated cycling, it is likely to be satisfctory in lab cells and larger cells. The test is not conclusive, since there has been at least one electrode which looked satisfactory by these criteria but evolved too much hydrogen when put into lab cells. We hope to improve our screening methods by varying the experimental conditions.

In building the 1-kW preprototype Redox system at Lewis Research Center, over 200 electrodes were prepared and individually tested by these methods. The electrodes were made slightly oversized and strips cut for testing. In some cases tests were run in small lab cells to verify the cyclic voltammetry results. The small cell results and the experience to date with the 1-kW system have confirmed that the above test procedure is a valid prediction of full-scale cell performance.

Discussion of cyclic voltammetry experimental setup and results. - In carrying out these screening experiments it became apparent that the details of the mounting and arrangement of the electrodes are very important. This is due to the nature of the felt electrode, that is, its high internal resistance compared to usual electrodes and its high internal surface area.

It was found that electrodes of different sizes, shapes, and mounting did not give the same types of voltammetry curves. Measurements of the internal resistance of the felt were made. Strips of felt of various widths and lengths were clamped between two electrode holders. For example, a strip 1.20 x 1.67 cm (the dimensions of the electrode used in these experiments) had a resistance in the lengthwise direction of about 2.3 . If this electrode is carrying a current of 50 mA (typical of peak currents in these experiments), there would be an IR drop from top to bottom of the electrode of 115 mV, that is, the voltage at the top of the active area would be significantly different from that at the bottom of the electrode. There is an additional IR drop in the 0.5 cm path from the top of the active area to the electrode holder. The current distribution would be affected by this and should be very nonuniform. From a number of resistance measurements on various pieces of felt, assuming the thickness of the loose felt to be about 80 mils, the volume resistivity of the loose felt was calculated to be about 0.3 Ω-cm (about 200 times that of graphite).

The net effect of the high resistance of the felt is that the potential between the working electrode and the reference electrode in the cells is not the same as the potential difference at the terminals of the potentiostat and is not the same at different points on the working electrode. Rather than try to correct for these effects, we have chosen to standardize the conditions of measurement. In order to minimize the resistance effects, we are now using electrodes of 1.41 x 1.41 cm. This sample size gave slightly better differentiation between the chromium and hydrogen reduction peaks. We chose not to go to smaller area electrodes or shorter, wider electrodes because this would introduce greater uncertainty in the active area due to slight variations in the amount of coverage by the hot wax used to mask the electrode holder and inactive felt area.

We also prefer to use an electrode of loose felt rather than compressing the felt in a holder. This compression will affect the contact resistance of the fibers in the felt, probably in a nonreproducible way. It will also affect the amount of electrolyte retained within the pores of the felt and thus modify the curves.

The effects of varying the resistance drop and compression of the felt are illustrated by the curves in figure 9.

Curve A shows the behavior of a good electrode in our usual experimental setup, with distinct separation of the chromium and hydrogen reduction peaks. A piece of the same electrode was used for curve B, but the electrode was a strip 0.55 cm wide x 7 cm long, the active (unwaxed) area being 0.55 cm x 3.65 cm (2 $cm^2$ area as before). The hydrogen and chromium reductin peaks are not well separated, and the current is much lower. In curve C we have an electrode of our usual size and shape (1.20 x 1.67 cm) but held in a coil of Ta wire. Again there is poor differentiation between the chromium and hydrogen peaks. By using an average value of resistance, corrections can be made to the above curves which bring them into closer agreement. However, since the resistance varies over the active area, this is only approximate. Another effect of the varying IR drop is that the true sweep rate is different at different points on the electrode and is not the same as that between the potentiostat terminals. The resistance effects, then, are very complex and will be difficult to analyze satisfactorily.

As mentioned earlier, when establishing a baseline by running cyclic voltammetry curves with $FeCl_3$, calculation of the area under the curve showed that essentially all the $Fe^{+3}$ contained within the pores of the felt was reduced on the cathodic sweep and the resulting $Fe^{+2}$ was oxidized on the anodic sweep. This and other experiments established that very little of the current can be accounted for by diffusion from the bulk of the solution. The reactions are essentially reactant-limited by the material within the pores of the felt. For a 2-cm$^2$ elctrode, about 0.42 cm$^3$ of electrolyte is retained if the electrode is not compressed. We assume from SEM and the capacitance measurements that the actual electrode area is at least 60 cm$^2$/cm$^2$ of projected area, so that the internal area of our electrode is about 120 cm$^2$. Thus the volume to area ratio (the average electrolyte thickness) is about 35 $\mu$. If we compare this to the 500 $\mu$ diffusion layer thickness usually found with stationary planar electrodes before convection sets in, it is obvious that the conditions are entirely different for this type of electrode. In the absence of any theoretical analysis of the voltammetry of such high resistance-high area electrodes, it is important to keep the experimental conditions constant in order to obtain data that can be used for quality control of the electrodes.

In our experimental setup, two counter electrodes were used at angles to the working electrode. The reference electrode was placed between the counter electrodes about 1 cm from the working electrode. No Luggin capillary was used. Changes in the position of the reference electrode of ±0.5 cm did not affect the curves. Good conductivity of leads and contacts was essential.

Variations in current with time and with different pieces of the same electrode were usually within about 10 percent, due to variations in the active area, amount of solution within the felt, and variations in the activity of the samples.

The amount of Pb used in the cyclic voltammetry experiments is much more than that used in the flow cells. In the flow cells one drop of saturated $PbCl_2$ is used per 10 cc of solution, which produces a concentration of about $6.25\times10^{-5}$ M. We used a different amount in the cyclic voltammetry experiments since in this case the solution is static rather than being pumped through the cells, and essentially only the $Pb^{+2}$ contained within the pores of the felt is plated onto the electrode. In the cyclic voltammetry experiments we add 50 drops of saturated $PbCl_2$ per 80 cc of solution; thus about 15 $\mu$g of Pb is deposited per cm$^2$ of felt, slightly more than the amount of Au present. This should be sufficient to cover all of the gold.

As discussed above, precise kinetic analysis of these curves is not possible since we are working with a porous felt rather than a smooth surface. Depletion of the active material will occur at different rates along the fibers depending on the distance between adjacent fibers. However, if we look at the cyclic voltammetry of the iron reactions, we find that the rate constant caculated from the peak separation at slow speeds gives us a value in reasonable agreement with rate constants determined by various methods on solid electrodes. The peak separation $\Delta E_p$ for an irreversible process is related to other parameters of the system by the expression

$$\psi = \frac{\gamma^{\alpha} k_S}{\sqrt{\pi a D_{OX}}} = f(n\,\Delta E_p)$$

where

$\psi$ = analytical function which has been tabulated for various values of $n \Delta E_p$ (ref. 7, pp. 338-343).
$n$ = number of electrons involved in the reaction
$D_{OX}$ = diffusion coefficient for the oxidized species
$D_{RED}$ = diffusion coefficient for the reduced species
$\gamma$ = $(D_{OX}/D_{RED})$
$\alpha$ = transfer coefficient
$k_S$ = standard rate constant in cm/sec
$a$ = $nF\nu/RT$ where $\nu$ is the sweep rate in V/sec. At 25° C, $a = 38.9\ n\nu$.

If we assume that $D_{OX} = D_{RED} \cong 1\times10^{-5}$ cm$^2$/sec, $n = 1$ and $\alpha = 1/2$ then

$$\psi \cong \frac{28.6\ k_S}{\nu^{1/2}}$$

Many studies have been made of the electrode kinetics of the iron Redox kinetics of the iron Redox reaction. The rate constant on carbon has been found to be between $1\times10^{-4}$ and $6\times10^{-4}$ depending on the nature of the carbon surface and the anions in solution (ref. 8). We have obtained cyclic voltammograms on our felt at a number of sweep rates. The peak separation at a sweep rate of 10 mV/sec corresponds to a rate constant of about $1\times10^{-4}$. At lower sweep rates of 1/2 to 1 mV/sec, the peak separation corresponds to a rate constant of about $6\times10^{-4}$. The voltammetry curves of chromium on well-catalyzed felt electrodes are similar to those of iron but with slightly smaller peak spearations. From the peak separation at low scan rates, the rate constant for the chromium Redox reaction is estimated to be about $1\times10^{-3}$ cm/sec, about 5 to 10 times as fast as the corresponding iron reaction. This is consistent with the polarization curves in figure 6(a). These indicate there is no appreciable voltage loss at either electrode due to activation. All voltage losses are attributable to IR.

Using the equations for peak height (ref. 7), an approximate value for the electrochemically active area of the felt can be calculated - about 65 cm$^2$/cm$^2$ of projected area. This compares well with a factor of 30 to 40 calculated from the average fiber diameter and density and a factor of about 60 estimated from the capacitance.

## CONCLUSIONS

The conclusions that can be drawn to date about Au-Pb catalyzed electrodes for the chromium side of the Redox storage system are as follows:

1. Satisfactory electrode performance is obtained at catalyst levels from 10 to 30 µg/cm$^2$ of Au and about 100 µg/cm$^2$ of Pb.

2. The pretreatment of the felt is very important. Earlier work indiated that the nature of the felt was important, that is, that variations from lot to lot were critical, but the newest methods of pretreatment combined with new deposition methods seem to be adequate to overcome most variations in the felt.

3. Electrodes plated in situ are not satisfactory because of reduction of the gold salts at reducing sites in or on the membrane. Colloidal gold electrodes do not look promising.

4. Thermal decomposition of gold salts seems best at present. Details of the procedure are very significant.

5. So far, used electrodes cannot be reused without excessive gassing. The reason for this is not known yet.

6. Cyclic voltammetry has been shown to be a useful screening method for Redox electrodes. Differences observed in the voltammetry scans can be correlated with the behavior observed in laboratory cells. Because of the high internal surface area of the felt and the high internal resistance, experimental procedures must be standardized in order to make meaningful comparisons.

7. Present methods for preparing electrodes seem entirely adequate for small cells, large single cells, and multicell stacks of 1/3 $ft^2$ size. Over 200 electrodes 1/3 $ft^2$ have been successfully tested for the 1-kW preprototype Redox energy storage system recently completed at NASA-Lewis. Whether further refinements will be needed for electrodes for larger stacks will be determined as scale-up proceeds.

8. The rate constant for chromium reduction on well-catalyzed felt is estimated to be about $1x10^{-3}$, about 5 to 10 times as rapid as iron reduction.

## Acknowledgments

The authors wish to thank Dr. Robert E. Post for the design of the electrode holder and for many helpful discussions.

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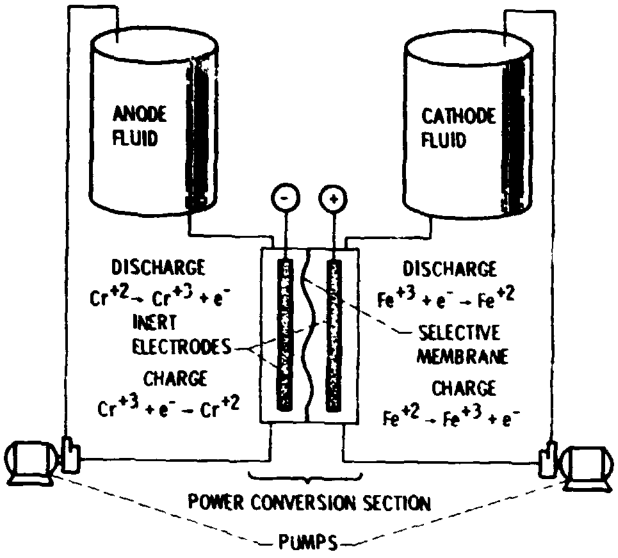


Figure 1. - Two tank electrically rechargeable redox flow cell.

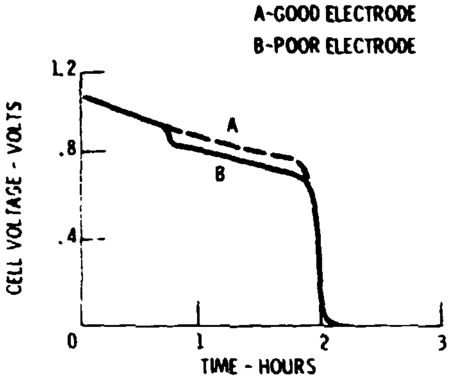
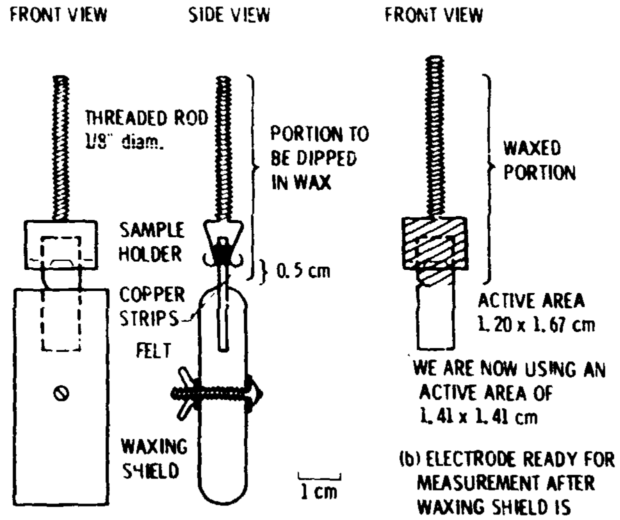
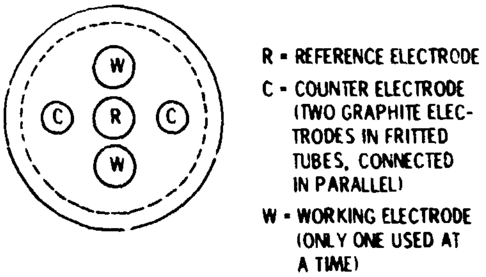


Figure 2. - Effect of electrode catalyst on discharge performance.



(a) ELECTRODE READY FOR WAXING.

(b) ELECTRODE READY FOR MEASUREMENT AFTER WAXING SHIELD IS REMOVED.



(c) TOP OF VOLTAMMETRY CELL.

Figure 3. - Electrode preparation and mounting.

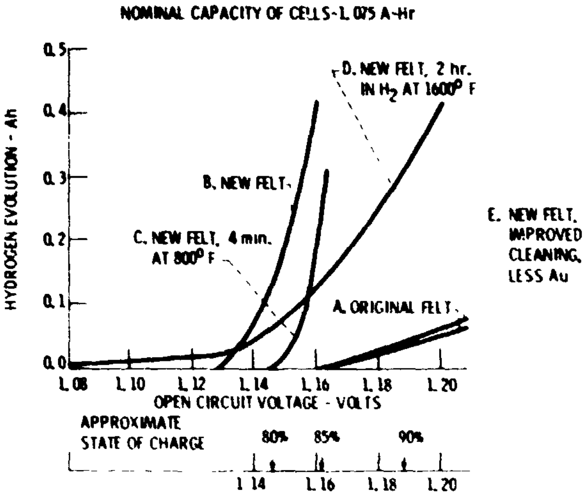


Figure 4. - Hydrogen evolved during charging of subscale cells.

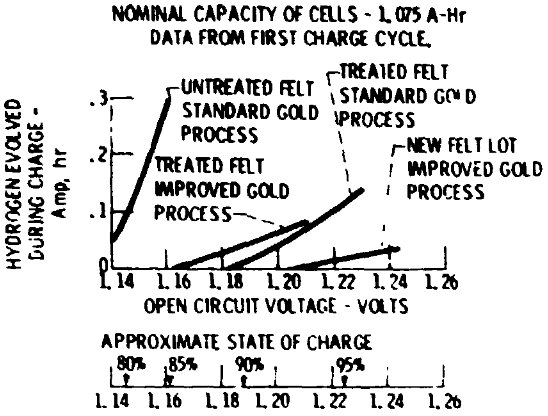


Figure 5. - Hydrogen evolution characteristics of improved chromium electrodes.

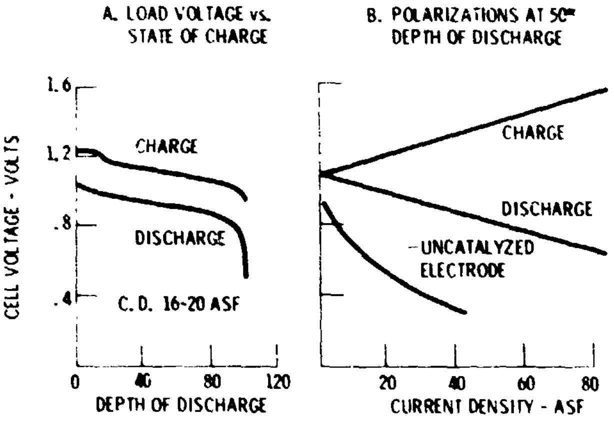
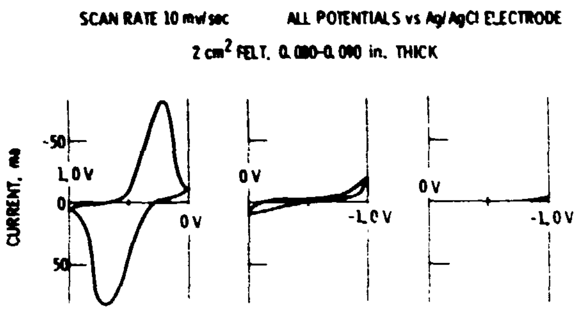


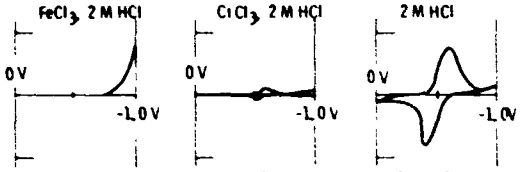
Figure 6. - Performance of 0.33 ft² single cell with best electrode and most conductive membrane.



A. UNCATALYZED FELT, 0.05 M $FeCl_3$, 2 M HCl

B. UNCATALYZED FELT, 0.05 M $CiCl_3$, 2 M HCl

C. UNCATALYZED 'GOOD' FELT, 2 M HCl

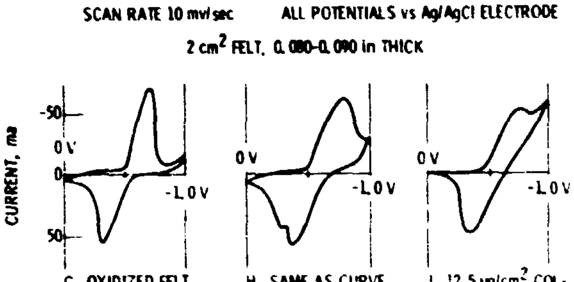


D. 'GOOD' FELT, 12.5 μg/cm$^2$ Au PLATED IN SITU, 2 M HCl

E. 'GOOD' FELT, 12.5 μg/cm$^2$ Au PLATED IN SITU, 2 M HCl WITH $10^{-4}$ M $PbCl_2$

F. 'GOOD' FELT, 12.5 μg/cm$^2$ Au PLATED IN SITU, 2 M HCl, WITH $10^{-4}$ M $PbCl_2$, 0.05 M $CrCl_3$

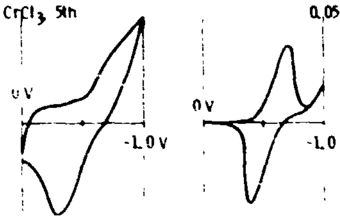
Figure 7. - Cyclic voltammetry of carbon felt electrodes.



G. OXIDIZED FELT, NO Au, $10^{-4}$ M $PbCl_2$, 2 M HCl, 0.05 M $CrCl_3$, 5th SWEEP

H. SAME AS CURVE G AFTER SEVERAL HOURS CYCLING

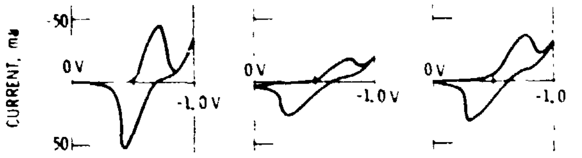
I. 12.5 μg/cm$^2$ COLLOIDAL Au, $10^{-4}$ M $PbCl_2$, 2 M HCl, 0.05 M $CrCl_3$



J. $HNO_3$ CLEANED POOR FELT 12.5 μg/cm$^2$ THERMALLY DEPOSITED Au, $10^{-4}$ $PbCl_2$, 2 M HCl, 0.05 M $CrCl_3$

K. BEST ELECTRODE $10^{-4}$ M $PbCl_2$, 2 M HCl, 0.05 M $CrCl_3$

Figure 8. - Cyclic voltammetry of carbon felt electrodes



A GOOD ELECTRODE, USUAL MOUNTING AND AREA R ~ 2 Ω

B. SAME ELECTRODE, 0.55 x 7.0 cm (ACTIVE AREA 0.55 x 3.65 cm) R ~ 10 Ω

C SAME ELECTRODE 1.20 x 167 cm IN Ta WIRE COIL HOLDER R ~ 3-5 Ω

Figure 9. - Effects of resistance and compression on cyclic voltammetry of carbon felt electrodes. Experimental conditions as before. Resistance is from contact to center of active area.