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PERFORMANCE OF ADVANCED CHROMIUM ELECTRODES
FOR THE NASA REDOX ENERGY STORAGE SYSTEM

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SUMMARY

E-1025

Significant advancements have been made in the chromium electrode used in the NASA Redox Storage System. Performance improvements have been achieved in single cell and stack hardware up to 930 cm^2 (1 ft^2) active cell area. Specific tests were developed to evaluate electrodes for hydrogen evolution, coulombic efficiency, catalyst stability and electrochemical activity. Performance of an electrode was found to be a function of the carbon frst lot, the cleaning treatment and the catalyzation procedure. Electrodes have been prepared which have low hydrogen evolution and reversible electrochemical activity to 108 mA/cm^2 (100 amps/ft^2).

Hydrogen evolution characteristics were determined by measuring the hydrogen liberated at the chromium electrode. The evolved hydrogen was discharged in a $\text{Fe}^{+3}/\text{H}_2$ rebalance cell, and the discharge coulombic capacity was measured to determine the quantity of hydrogen produced. In general, hydrogen evolution on an improved electrode was less than 1 percent of net charge when the $\text{Cr}^{+2}/\text{Cr}^{+3}$ redox couple was charged to about 80 percent state-of-charge. Coulombic efficiency for a charge/discharge cycle between 0 and 80 percent state-of-charge was measured to be about 98 percent for a single cell with an improved electrode.

Catalyst stability was determined through rapid cycling and cell reversal tests. These tests exercise the catalyst under severe electrochemical conditions. The rapid cycling technique charges and discharges only the reactant fluid retained within the porous carbon felt electrode under no-flow conditions. About 100 cycles can be accomplished per day. Cell reversal tests place the chromium electrode under severe electrooxidative conditions by driving the cell to negative operating voltages. Detrimental changes in the nature of the catalyst are generally evidenced by increased hydrogen evolution. An improved electrode has shown low hydrogen evolution after cell reversals to -1.1 volts and 20,000 rapid cycles indicating excellent catalyst stability.

Electrochemical activity of an electrode for the oxidation and reduction of the chromium solution was determined from cell polarization tests and constant current/constant voltage cycling. Polarization curves at various states-of-charge indicate reversible electrode behavior.

Electrodes having the best performance had received a hot KOH cleaning treatment, and were then impregnated with an aqueous methanol gold salt solution, which was then thermally decomposed. Lead was then electrochemically deposited on the gold. However, this procedure has not been as successful with all lots of carbon felt. A "standard" cleaning treatment and catalyzation procedure has not yet been established which will produce acceptable electrodes from any lot of carbon felt.

Impurities in the chromium solution were found to have a detrimental effect on the electrode performance. Controlled amounts of Fe, Al, Ca, V and Mg

appeared to make the lead catalyst ineffective leading to higher hydrogen evolution. Use of a technical grade of chromic chloride resulted in the development of kinetic polarizations.

INTRODUCTION

The NASA-Redox Energy Storage System has become a leading candidate as an electrochemical method for bulk electrical energy storage (refs. 1 to 3). Under development since 1974, the technology has progressed steadily and the Redox system is currently considered cost competitive with lead-acid batteries as an electrochemical bulk energy storage device.

NASA-Redox Storage System

Reactant solutions of acidified iron chloride and chromium chloride, which are stored in external tanks, are circulated through a stack(s) of cells. The reactants, separated by semi-permeable membranes in the cells, are electrochemically reduced or oxidized on inert electrodes to store and produce electricity. During charging, the energy to be stored (from photovoltaic cells, e.g.) is used to oxidize the iron solution to ferric ion while the chromium solution is reduced to chromous ion. During discharge, the reverse spontaneous reactions occur as the ferric ion is reduced to ferrous and the chromous ion is oxidized to chromic. The electrical energy produced during discharge is used to power an external load.

Specific technology areas under development are electrodes (refs. 4 and 5) membranes (refs. 6 and 7), cell designs (ref. 8) and multicell systems (ref. 9). Single cell and multicell units of up to 930 cm² (1 ft²) per cell have been constructed and tested. System performance meets the storage performance requirements for photovoltaic and wind turbine applications based on power densities and solution crossover rates. However, further improvements are necessary to meet the system requirements for electric utility load leveling applications. The content of this paper focuses on chromium electrode development.

Cr Electrode Requirements

The electrode for the Redox system must be an inert material with sufficient surface area and good electrochemical activity for the oxidation and reduction of the chromium and iron solutions. Since the reduction of Cr⁺³ to Cr⁺² in the presence of H⁺ is not favored thermodynamically, a catalyst must be applied to the electrode substrate to provide selective reduction of the Cr⁺³. The addition of a Au/Pb catalyst to a carbon felt material has been shown to give good electrochemical activity for chromium reduction and oxidation while minimizing H⁺ reduction during charge (ref. 4).

Various materials have been evaluated as electrodes and electrode substrates. The most favorable characteristics have been obtained with carbon and graphite felts. Carbon felt has been preferable because of its greater physical strength and surface area, thickness, availability and cost. The development of the Cr electrode has been plagued by the variability of properties of carbon felt lots delivered by the manufacturer. Each lot has exhibited different characteristics toward the Au/Pb catalyzed process (ref. 4). Differences in physical properties; e.g., density, surface area, wettability and oxidation resistance have been observed. Apparently, surface properties

of the carbon fibers vary greatly depending on temperature and atmospheric conditions during felt processing.

Cr Electrode Catalyzation

Gold catalyzation of the carbon felt substrate material has been done by thermal or electrochemical reduction of gold ion onto the carbon fibers. Although both methods have produced satisfactory electrodes, thermal plating has generally been used. Very small amounts of gold and lead are adequate to provide electrochemical activity for the chromium oxidation/reduction reactions. The quantity of lead required to catalyze the electrode is added to the chromium reactant solution and electrochemically reduced onto the gold catalyzed carbon felt.

Typically, chromium electrodes must have good activity for chromium oxidation and reduction but not for hydrogen evolution. These catalysts must also remain stable after extended periods of cycling over wide ranges of depth-of-discharge. Another condition under which an electrode must be unaffected is during periods of cell reversal (i.e., a negative voltage impressed on the cell). Negative cell voltages can occur in multicell stacks during periods of no reactant flow (e.g., overnight shutdown, maintenance, etc.): The center cells of a stack can be driven to negative voltages because of internal shunt currents through the solution manifolds. Since shunt current effects are greatest in the center of a stack, these chromium electrodes undergo electrooxidation conditions which could change the nature of the catalyst surface.

Cr Electrode Evaluations

Specific tests were developed to characterize carbon felts, cleaning treatments and gold catalyzation procedures. In-cell electrode evaluation measurements include polarization tests, hydrogen evolution rate and coulombic efficiency during cell reversal, rapid cycling and full cycling tests. Cyclic voltammetry was used in an out-of-cell evaluation method and is described in reference 4.

Hydrogen evolution is a main criterion in determining an acceptable electrode. The goal for acceptable electrode performance is that the hydrogen evolution be equivalent to less than 1 percent of the total coulombic capacity from 0 to 80 percent state of charge. Hydrogen evolution characteristics are determined by quantitatively measuring the hydrogen evolved during a cycle, through the use of a rebalance cell (ref. 1). The discharge current from the $Fe^{+3}/Fe^{+2}/H_2/H^+$ reaction is measured with an amp-hr integrator to measure hydrogen generated as a function of state-of-charge.

Cycle coulombic efficiency, as used in this report, is the measured ratio of amp-hrs generated during the discharge portion of the cycle divided by the amp-hrs required for charge. This efficiency is generally directly related to the hydrogen evolution, but could also indicate side reactions involving catalysts and/or reactants.

Cell reversal and rapid cycling tests are used to determine the stability of the catalyzed electrode. Cell reversal causes the electrode to undergo severe electrooxidation conditions. For reversal testing, the cell is "over-discharged", using a power supply to drive the cell voltage and open-circuit voltage negative in an attempt to strip the catalyst from the porous carbon substrate. This polarity reversal for open-circuit voltage is possible because forced discharge oxidizes any Fe^{+2} present in the chromium solution to

Fe^{+3} and reduces any Cr^{+3} present in the iron solution to Cr^{+2} . Removal of the catalyst or a change in catalyst structure could cause performance changes. Rapid cycling is an accelerated cycling technique in which the pumps are stopped and only the nonflowing reactant solutions within the cell cavity are charged and discharged. About 100 cycles per day are possible between 10 and 90 percent depth-of-discharge. To ascertain what performance change, if any, took place during cell reversals and rapid cycle testing, full cycling tests (pumps running) are performed periodically to re-evaluate the hydrogen evolution and voltage/current polarization characteristics.

Small electrode samples are tested by cyclic voltammetry (ref. 4). The electrochemical activity of an electrode is determined by applying a variable voltage and measuring the current response as a function of time. Electrode performance as a function of solution concentration and catalyst loading can be determined. Correlation with full-scale single cell tests is also made.

The purpose of this work is to develop a catalyzed carbon felt electrode which is stable to anodic voltages, has good chromic ion reduction characteristics and low hydrogen evolution rates. Procedures are described for treating and catalyzing carbon felt to produce chromium electrodes. Test procedures for determining hydrogen evolution, catalyst stability and oxidation/reduction activity are also described along with results from several of the improved electrodes. The effects of chromium solution impurities on electrode performance are also determined.

PREPARATION OF ADVANCED ELECTRODES

Substrate Material Requirements

An inert, electrically conductive material of sufficient surface area is required as a substrate for the Redox reactions. Porosity must be high to minimize pressure drop across the electrode, but the material must possess suitable compressibility characteristics to make proper electrical contact with the bipolar conductive plate behind it. Numerous materials of carbon/graphite composition have been tested. These include felts of various thickness, cloths, papers, chemically vapor deposited felt, foams, vitreous carbon and rigidized fiberboard type materials. Felt has primarily been used since it meets the above requirements and is readily adaptable to multicell stack applications because of its compressibility. For most single cell applications and all multicell stacks, 3.2 mm (1/8") carbon felt has been used and meets the above criteria.

Other substrates such as refractory metal screens have been used but have not been successful.

Cleaning treatment. - Due to apparent variations in surface activity of carbon felt lots, numerous surface wetting and cleaning treatments have been used. Soaking in methyl alcohol, ethyl alcohol, isopropyl alcohol or acetone were used to provide for fiber wettability prior to additional cleaning treatment and catalyzation. Following wetting with a nonaqueous solvent, the felt is water rinsed and partially dried on absorbent toweling. The felt is then soaked in hot (90° C) solutions of potassium hydroxide, hydrochloric acid, sulfuric acid, nitric acid or chromic acid. This treatment removes metallic impurities, organic hydrocarbon residues and in some cases modifies the surface activity of the fibers. The primary purpose of the cleaning treatment is to make the felt as uniform as possible so that catalyst application is controlled and electrodes with reproducible characteristics can be prepared.

A treatment which would normalize the felt from different lots is desirable but has not been successfully accomplished as yet.

Catalysis procedure. - Gold and lead catalysts have been applied to the carbon felt substrate by several techniques. Gold can be applied alone as a chloride salt solution and then reduced to metallic gold by electrochemical reduction or by reducing the gold oxide at an elevated temperature. Gold and lead have also been applied together by electrochemical coreduction. Impregnation of the felt with gold has been most successfully accomplished by soaking the felt in an aqueous methanol gold chloride solution. The felt is then dried at 100° C, followed by heating in air at 260° - 270° C for 2 hr. After the cell is assembled, trace amounts of lead are added to the chromium reactant solution and electrochemically reduced on the electrode at a low current density. Although both electroplated gold electrodes and thermally reduced gold plated electrodes have given good electrochemical performance, the thermal treatment has been preferred due to more specific distribution of the gold.

Typical electrode preparation procedure. - A detailed description of the procedure used to process the as-received carbon felt to produce a catalyzed chromium electrode is given in the Appendix.

ELECTRODE TESTS

Electrodes are tested in 14.5 cm² (0.0156 ft²), 310 cm² (0.33 ft²) and 930 cm² (1 ft²) hardware. A 310 cm² half cell is shown in figure 1. A cell consists of two such identical cell halves separated by a highly selective ion exchange membrane. The electrode is placed in the flow field/gasket cavity and compressed between the membrane on one side and the graphite plate current collector on the other. One inch thick polyvinylchloride insulator plates are used to carry solutions into the cell cavities. One-half inch thick steel end plates are placed on the outside of the cell to uniformly distribute tie-rod forces.

Automated Testing Equipment

Automated test stands were constructed to automatically cycle a Redox cell between preselected voltage limits. Either the cell operating voltage or the open-circuit voltage can be used to control the cycling. Schematic diagrams of the electrical and hydraulic systems are shown in figures 2 and 2A, respectively. In order to control the system by the open-circuit voltage, an open-circuit cell is placed in series hydraulically with the test cell. A Fe³⁺/H₂ rebalance cell is also used in most tests to maintain electrochemical balance between the reactant solutions and to measure the hydrogen liberated at the chromium electrode. The rebalance cell is a valuable analytical tool for determining the hydrogen evolution characteristics of the electrodes as a function of the state-of-charge. Amp-hr integrators monitor both the test cell and the rebalance cell. A constant current/constant voltage power supply is used to both charge and discharge the test cell. Discharging can also be done through a resistive load.

Several types of pumps are used to circulate the reactant solutions depending on the particular test. Bellows pumps are satisfactory for circulating solutions for tests insensitive to intermittent flow. Magnetically-coupled centrifugal pumps are used for continuous flow requirements. Variable flow metering pumps are used for flow study applications. Components of the pump in contact with the reactant fluids are fabricated from polypropylene, Teflon or ceramic. Solution reservoirs are made of glass, polyethylene or

polypropylene. Connecting tubing is a polyethylene lined type which provides corrosion resistance and good flexibility.

Hydrogen Evolution Evaluation

The electrochemical reduction of hydrogen ion to hydrogen gas at the chromium electrode during charging represents a loss in cycle coulombic efficiency. Thus, it is desirable to have electrodes which have low hydrogen evolution characteristics, but still retain good chromic ion reduction activity. The amount of hydrogen evolved during a cycle is measured with a $\text{Fe}^{3+}/\text{H}_2$ rebalance cell. The rebalance cell and its relationship to the test system is shown in figure 2A. Hydrogen evolved at the chromium electrode is trapped in the chromium solution reservoir. Here the gas diffuses into the attached rebalance cell and is oxidized on a platinized carbon electrode. Ferric ion is reduced on a carbon felt electrode in the other half of the cell. The cell is short-circuited through an amp-hr integrator which quantitatively measures the evolved hydrogen. This permits the measurement of the amount of hydrogen evolved as a function of the state-of-charge, and during a complete cycle.

Coulombic Efficiency Determination

An amp-hr integrator connected in series with the test cell is used to measure the charge and discharge capacity of the system. Comparisons are made of the measured capacity with the theoretical coulombic capacity of the reactant solutions. The ratio of discharge capacity to charge capacity gives the efficiency for a particular cycle. Factors possibly affecting the coulombic efficiency include electrochemical hydrogen evolution, chemical hydrogen evolution due to hydrogen ion reduction by chromous ion in the bulk solution, oxygen leakage into the system, ionic short circuit due to membrane cross-leakage, electrical shorting between the anode and cathode current collectors and irreversible electrochemical reactions.

Rapid Cycling Tests

This technique was developed to accelerate the electrode changes which occur during charging and discharging. The performance of the chromium electrode is dependent on the stability of the gold and lead catalyst deposited on the carbon felt. The cells are cycled at an accelerated rate by turning off the solution circulating pumps and cycling only the reactant fluid trapped in the cell cavity between 10 and 90 percent DOD. Periodically the solutions are briefly circulated through the cell to correct for chemical imbalance due to hydrogen evolution and for iron-chromium crossmixing. About 100 cycles per day can be done on the 14.5 cm^2 (0.0156 ft^2) and the 0.310 cm^2 (0.33 ft^2) cells. Discharge current density is 22 mA/cm^2 (20 amps/ft^2). Charging current density begins at 22 mA/cm^2 (20 amps/ft^2) but tapers as the cell reaches the 1.25 volt limit.

Cell Reversals Test

These tests were also used to determine catalyst stability. The test cell is driven to negative voltages in order to subject the chromium electrode catalysts to strong electrooxidation conditions. Following a complete discharge (100 percent DOD) using a power supply, the cell voltage and the open-

circuit voltage are taken stepwise to a -1.1 volts. This polarity reversal for open-circuit voltage is possible because forced discharge oxidizes any Fe^{+2} present in the chromium solution to Fe^{+3} and reduces any Cr^{+3} present in the iron solution to Cr^{+2} . There is no evidence that chlorine is generated during the reversal. The system is then charged back to zero open-circuit voltage and normal cycling resumed between 10 and 90 percent DOD. Hydrogen evolution is again measured with the rebalance cell as a function of state-of-charge.

Polarization Tests

The electrochemical activity of a particular electrode is determined by measuring its voltage-current relationship up to 108 mA/cm^2 (100 amps/ft^2). These tests are performed, using the automated test stand by applying the required current in the charge or discharge mode for about twenty seconds. The degree of linearity of the curves of voltage as a function of current density indicates whether the electrode has kinetic or concentration polarizations. Kinetic effects and poor mass transport properties of an electrode are evidenced by nonlinearity at low current densities (1 to 20 mA/cm^2) and high current densities (70 to 100 mA/cm^2), respectively. The slope of the discharge performance is a measure of the cells internal resistance. Cell resistance is also measured experimentally with an impedance bridge at 1000 Hertz. This measurement generally is in good agreement with the resistance calculated from the slope of the voltage-current relationship.

Reactant Impurity Tests

Three experiments were performed on chromium solutions with different levels of impurity to determine possible electrode poisoning and/or membrane fouling effects. Hydrogen evolution and polarization performance tests were used to evaluate the magnitude of such effects.

The effect of impurities in reagent grade chromic chloride was studied by using a system having a large volume of reactant solution in comparison to the electrode and membrane area. One liter of reactant solution was tested with a 14.5 cm^2 single cell. (Reactant volume/membrane or electrode area of $70 \text{ cm}^3/\text{cm}^2$. This volume to area ratio is consistent with a solar energy/Redox storage application.) Although present only in trace amounts, impurities from the solution could be concentrated on the electrode or membrane causing changes in cell performance.

Next the effects of specific impurities on electrode performance was determined by preparing a chromium solution "doped" with known amounts of impurities expected to be present in a chromium solution prepared directly from chromite ore. (It is anticipated that chromium reactants produced directly from chromite ore would be of an acceptable low cost.) The composition of this solution was: 1 M CrCl_3 , 2 M NHCl , 0.05 M FeCl_2 , 0.05 M AlCl_3 , 0.1 M CaCl_2 , 0.05 M MgCl_2 and 0.01 M V_2O_5 . The solution was cycled in a 14.5 cm^2 single cell using a Au/Pb catalyzed chromium electrode and a solution to area ratio of $2.8 \text{ cm}^3/\text{cm}^2$.

A third test to measure the effect of impurities in the chromium solution was conducted with a commercially available, technical grade, 62 percent liquid chromic chloride. (Technical grade chromic chloride also represent a reduced cost compared to reagent grade.) The chromium concentration was adjusted to one molar and the hydrochloric acid concentration to two molar. Cy-

cling was done in a 14.5 cm^2 single cell using 40 cm^3 of chromium solution. (Volume/area = $2.8 \text{ cm}^3/\text{cm}^2$)

RESULTS AND DISCUSSION

Hydrogen Evolution Rate

Figure 3 illustrates the differences in hydrogen evolution during the first cycle, for electrodes prepared from two felt lots using different cleaning treatments and gold catalyst application processes. Hydrogen evolution characteristics are found to be sensitive to the carbon felt lot, the cleaning treatment, and the method of applying the gold onto the carbon felt fibers. A hydrogen amp-hr value of 0.1 represents about 10 percent of the reactant solution capacity. Electrode no. 1, which was "as-received" felt, began producing hydrogen below an open-circuit voltage (OCV) of 1.14 volts and produced 0.3 amp-hr of hydrogen when catalyzed by the standard gold catalyzation procedure. When this same felt was treated in hot nitric acid (electrode no. 2) prior to catalyzation, hydrogen evolution did not begin until the OCV reached 1.16 volts. Total hydrogen liberated by this electrode was about 0.08 amp-hr when charged to 93 percent state-of-charge. Electrode no. 3 also was from the same felt lot and treated in hot nitric acid, but catalyzed with an alcoholic gold solution. The threshold for hydrogen evolution was increased to 1.18 volts OCV. Total hydrogen generated was 0.15 amp-hr (14 percent) when the cell was charged to 96 percent. Electrode no. 4 was prepared from a new lot of felt using a hot KOH cleaning treatment followed by catalyzations with alcoholic gold solutions. This electrode did not begin gassing until 1.20 volts OCV and produced 0.04 amp-hr (3.7 percent) when charged to 97 percent state-of-charge. It should be noted that, in normal operation, Redox cells would not be charged to such high levels. 90 percent state-of-charge would probably be the maximum.

Catalyst Stability

The use of rapid cycling provides a convenient method for accelerated testing of the various electrodes. With this technique, the solution pumps are shut down and the cell is automatically cycled to oxidize and reduce as rapidly as possible the reactant solutions retained within the cell. A graphical representation of rapid cycling is illustrated in figure 4. Cycling is regulated between upper and lower voltage limits equivalent to 10 and 90 percent depth-of-discharge. Rapid cycling is usually done at current densities of 11 to $22 \text{ mA}/\text{cm}^2$ (10 to $20 \text{ amps}/\text{ft}^2$) to simulate operating conditions of proposed larger systems. All cycles are uniform unless the electrode is prone to hydrogen evolution. This causes solution imbalance to develop and the cycles progressively become shorter. When this occurs, occasional solution circulation is required. Periodically (every 500, 1000 or 2000 rapid cycles), polarization tests are done on the cell to determine the reproducibility of electrode performance, which is a measure of the catalyst stability.

Cell reversal tests provide a second method for determining catalyst stability. The cell is taken stepwise to increasingly more negative voltages, each time followed by a normal cycle to indicate any change in hydrogen evolution characteristics or polarization performance. Results of polarization tests for a 310 cm^2 (0.33 ft^2) cell following 12 reversals and 20,000 rapid cycles at 50 percent depth-of-discharge are shown in figure 5. This electrode was cleaned in hot KOH and catalyzed with an alcoholic gold solution to $13 \mu\text{g}$

Au/cm². Reversal tests were begun at -0.1 volt and continued to -1.1 volts in 0.1 volt increments. Amp-hr efficiency for the normal cycle following each reversal cycle was always greater than 95 percent, with no change in hydrogen evolution. Following reversal testing, this improved electrode was rapid cycled. Polarization tests were run periodically to 108 mA/cm² (100 amps/ft²) and showed no change from the initial performance (except for IR) through 16,000 cycles. At this point, discharge curves remained unchanged, however, the charge curve showed voltage deviations at current densities greater than 65 mA/cm² (60 amps/ft²) when compared to the new electrode. The nature of the catalyzed electrode surface apparently changed slightly although continued cycling through full cycles gave no greater hydrogen evolution. The 20,000 rapid cycles represents more than 50 years of operation for a storage system on a daily cycle basis.

An electrode prepared from another lot of carbon felt using an aqueous gold catalyzed process had hydrogen evolution less than 1 percent before undergoing a cell reversal. Following one reversal cycle to -0.7 volt, hydrogen evolution began at only 1.0 volts OCV on a normal cycle. Total hydrogen evolved was 4 percent when taken to 80 percent state-of-charge. Attempts to restore the original electrode performance by adding more lead to the chromium solution were unsuccessful.

Performance at Various States-of-Charge

Performance of an improved electrode during full cycling was determined from polarization tests at various DOD's. Polarization tests made on a 310 cm² (0.33 ft²) electrode at 25, 50 and 75 percent DOD are shown in figure 6. Charge and discharge performance at 25, 50 and 75 percent DOD showed no evidence of kinetic polarization. However, charging at 25 percent DOD did lead to non-linear performance, probably due to mass transport at the higher current densities. Also, generally above 1.5 volts, hydrogen evolution becomes significant and considerable voltage fluctuation is observed. Once profuse gassing begins, the cell voltage stabilizes.

Open-Circuit Voltage Hysteresis

During full cycle testing of chromium electrodes, it was observed that at above 50 percent SOC, different OCV's were obtained depending on whether the system was being charged or discharged. Figure 7 gives an illustration of this hysteresis effect. This was a 310 cm² (0.33 ft²) electrode cycled at 22 mA/cm² (20 amps/ft²). The system had a reactant-volume-to-membrane-area ratio of 0.65 cm³/cm². A second observation, made during full cycling, was the color change of the chromium solution. During charging of chromium solutions prepared with 2 N HCl, the color changes from a dark bluegreen in the completely discharged state to blue-green at about 25 percent SOC, followed by a dark blue color at about 50 percent SOC. Above 50 percent SOC, the solution gradually becomes a lighter blue color. Generally, above about 60 percent SOC, the OCV is not stable, tending to gradually drift downward. As the cell is discharged, the chromium solution color changes from light blue to light green blue within the first 10 to 20 percent of the discharge (independent of the final charged SOC) instead of returning to the darker blue color. The light green-blue color gradually darkens as the chromium solution is further oxidized. When the system is completely discharged, the chromium solution has returned to its original dark blue-green color. The degree of hysteresis was found to depend on the ratio of reactant volume to membrane area. This effect

has been observed with all electrodes in varying degrees, but the effect appears less in systems having high reactant-volume-to-electrode - membrane-area ratio.

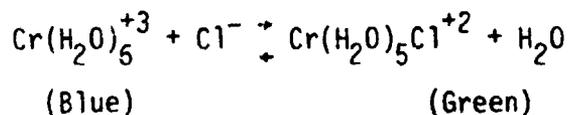
Electrode Preparation Effects

Full cycle testing also was used to evaluate performance differences of various electrode preparation methods. Figure 8 shows a comparison of electrode no. 1 prepared using a KOH cleaning treatment and aqueous methyl alcohol gold catalyzation, and electrode no. 2, prepared using an HCl cleaning treatment followed by aqueous ethyl alcohol gold catalyzation. Both electrodes had a reactant volume/membrane area ratio of 1.63 cm³/cm² and were charged at 22 mA/cm² (20 amps/ft²) constant current. The cell voltage was allowed to increase until significant hydrogen evolution occurred. Charging was terminated at this point since no increase in state of charge was obtained. Internal resistance for both cells was identical. The difference in effectiveness for charging the chromium solution can be seen by the voltage separation between the voltage curves. These results indicate electrode no. 1 is more effective than electrode no. 2 for the reduction of Cr⁺³ to Cr⁺². The higher the SOC that can be obtained before the rapid rise in voltage and hydrogen evolution occurs, the better the electrode.

Charge Acceptance

Figure 9 shows the results of charge acceptance tests for an improved electrode. Constant voltage was applied to the cell and the cell current measured as a function of SOC. Reactant volume/membrane area was 1.63 cm³/cm². Good charge acceptance was obtained to about 60 percent state-of-charge with low hydrogen evolution. However, at this point the charging current decreases rapidly and, for voltages greater than 1.4 volts, there is considerable H₂ evolution. This rapid loss in charging current is attributed to the hysteresis effect and is thus more pronounced in systems having low volume/area ratios. A comparison of this system (volume-to-area ratio of 1.6) is made in figure 10 with a system having a ratio of 70. A large improvement in charge acceptance is observed above 60 percent SOC for the latter system.

The proposed explanation for these phenomena takes into consideration the ionic species present in the chromium solution. It is well known that aqueous chromium chloride solutions contain numerous complex ion species depending on the acidity and salt concentrations. In the presence of hydrochloric acid, the predominant species are the hexaquachromium III ion, Cr(H₂O)₆⁺³, and the pentaquachlorochromium III ion, Cr(H₂O)₅Cl⁺². The predominating equilibrium established is:



Kinetic studies have shown that the Cr(H₂O)₅Cl⁺² ion is more readily reduced to the chromous state than is the Cr(H₂O)₆⁺³ ion (ref. 10). Therefore, the following explanation is proposed for the observed hysteresis. Starting with a freshly prepared 1 MCrCl₃ solution in 2 NHCl, the color is green and the major species is Cr(H₂O)₅Cl⁺². As the system is charged, the Cr(H₂O)₅Cl⁺² is reduced to the Cr⁺² state. The solution thus gradually loses its green color and changes to deep blue, which is the color of the Cr(H₂O)₆⁺³ species. (Cr⁺²

solutions are light blue.) Since the $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ is a more stable ion, the cell open-circuit voltage rises as this ion becomes predominant. To maintain a constant charge current therefore requires an increase in applied cell voltage. As the system is discharged, the light blue Cr^{+2} is oxidized to the lower voltage specie, $\text{Cr}(\text{H}_2\text{O})_5 \text{Cl}^{+2}$ which is green and which has associated with it, at a given SOC, a lower OCV than for the charging situation. However, with time the two oxidized species tend toward equilibrium. These considerations account for the higher open-circuit voltage during charge (fig. 7) and the accompanying sudden decrease in charging current observed (fig. 9) at about 60 percent SOC under constant voltage conditions. Also, from the results shown in figure 8, it is apparent that electrode no. 1 provided a better catalytic surface for the chemical equilibrium to favor formation of the $\text{Cr}(\text{H}_2\text{O})_5 \text{Cl}^{+2}$ species.

Reactant Impurity Effects

Electrode poisoning and membrane fouling could occur when impurities, although in low concentration in the solutions, are electrochemically deposited on the electrode or absorbed on the membrane. When this occurs, the electrode may become irreversible or the membrane resistance may increase. Polarization results for a system with a large reactant-volume-to-membrane or electrode area ratio of $70 \text{ cm}^3/\text{cm}^2$ are shown in figure 11. These results indicate no apparent electrode poisoning effects between 10 and 90 percent state-of-charge. Differences in slopes can be attributed to resistance changes over the extended cycling period, but no significant membrane fouling was observed. "Analyzed Reagent" grade chemicals were used for this study, so even with the relatively large volume of reactant, the total impurity content was low.

The results of polarization tests at 50 percent DOD for a purposely contaminated chromium solution are shown in figure 12 and indicate reversible electrode performance. However, an unacceptable amount of hydrogen was produced at the chromium electrode. Apparently, some of these particular impurities in the chromium solution are electrodeposited over the lead catalyst producing an electrode surface with a low hydrogen overvoltage. No significant cell resistance increase was observed, indicating minimal membrane fouling effects by the impurities.

The third test to measure the effect of impurities in the chromium solution was conducted with a technical grade, 62 percent liquid chromic chloride. Results of polarization tests are shown in figure 13 and compared with results for reagent grade chromic chloride. Large kinetic polarization effects were observed which are probably caused by dissolved impurities poisoning the catalyzed surface. (Spectroscopic analysis of the solution indicated a high silicon content.)

From the above results it is apparent that some impurities can adversely affect the performance of the chromium electrode.

CONCLUSIONS

Gold-lead catalyzed carbon felt was demonstrated to be a satisfactory chromium electrode for the NASA-Redox Storage System. Electrodes with very low hydrogen evolution, excellent catalyst stability, and reversible electrochemical activity were prepared. Gold and lead loadings of $13 \mu\text{g}/\text{cm}^2$ and $100 \mu\text{g}/\text{cm}^2$, respectively, were adequate to meet the performance requirements.

Specific in-cell tests were developed to evaluate the catalyzed elec-

trodes. The $\text{Fe}^{+3}/\text{H}_2$ electrochemical rebalance cell proved to be a valuable tool for measurement of the hydrogen evolved from the electrode during cycling.

Charging cells at a specific constant current differentiated electrodes in term of chromic ion reduction activity.

Cell reversal and accelerated cycling tests were used successfully to determine catalyst stability.

An open-circuit voltage hysteresis phenomenon was observed and is attributed to several different ionic species in the chromium solution. Major species present are the pentaquachlorochromium III ion, $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{+2}$, and the hexaquachromium III ion, $\text{Cr}(\text{H}_2\text{O})_6^{+3}$. Above about 50 percent state-of-charge, during the charge portion of a cycle, the $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ ion is the major specie present. However, during the discharge portion of the cycle, down to about 50 percent DOD, formation of the $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{+2}$ species is predominant. The difference in open-circuit voltage as a function of DOD is attributed to the different half cell potentials of the two species. The performance differences observed between electrodes during constant current cycles were attributed to catalyst activity differences for the particular electrodes affecting the equilibrium between the two ionic species. Reasons for the differences in catalytic activity have not been determined.

Certain impurities possible in the chromium solutions were shown to have a detrimental effect on electrode performance. Increased hydrogen evolution and reaction kinetic effects resulted.

In general, electrode performance was dependent on the particular carbon felt lot, the cleaning treatment and the catalyzation procedure. A common procedure has not yet been established for treating all carbon felt lots to produce acceptable electrodes. Nonetheless, electrodes were prepared which maintained their initial performance after strong electrooxidation cycles, thousands of rapid cycles and hundreds of full cycles.

APPENDIX

Summary of typical procedure for chromium electrode preparation. - The following is a procedure which has produced chromium electrodes with excellent electrochemical performance from several lots of carbon felt. Although this is not a "universal" procedure for any commercially available carbon or graphite felt, several hundred electrodes with reproducible characteristics have been fabricated from one felt lot.

- (1) Soak in methyl alcohol to wet the felt.
- (2) Rinse well with deionized water and damp dry on absorbent towel for five minutes.
- (3) Place in 45 percent potassium hydroxide solution at 90° C for two hours.
- (4) Rinse thoroughly in tap water, then deionized water. Soak overnight in deionized water.
- (5) Prepare catalyst solution as follows for each 100 cm² of 1/8" carbon felt:
 - (a) 5 cm³ of 1.27 10⁻³ N aqueous gold chloride
 - (b) 15 cm³ of methyl alcohol
 - (c) Mix the two solutions just prior to use
- (6) Damp dry felt for two minutes on absorbent toweling.
- (7) Pour one-half of catalyzing solution into a glass or plastic tray with same approximate dimensions as the felt.
- (8) Lay damp felt in tray and physically manipulate solution into the felt.
- (9) Lift electrode out of tray, pour excess solution into a beaker and pour second half of catalyzing solution into tray.
- (10) Turn electrode over and repeat step 8.
- (11) Place electrode in a plastic bag, seal, and allow to stand overnight.
- (12) Remove from bag and dry on a glass plate at 100° C.
- (13) Place in a 260° C furnace for 2 hours.

The electrode is now ready to be placed in a cell. Just prior to use, the electrode is dampened with water and placed in the Redox cell. Chromium solution containing a trace of lead chloride solution is circulated through the cell. The cell is charged at 0.3 mA/cm² to reduce lead onto the surface of the gold catalyzed carbon felt.

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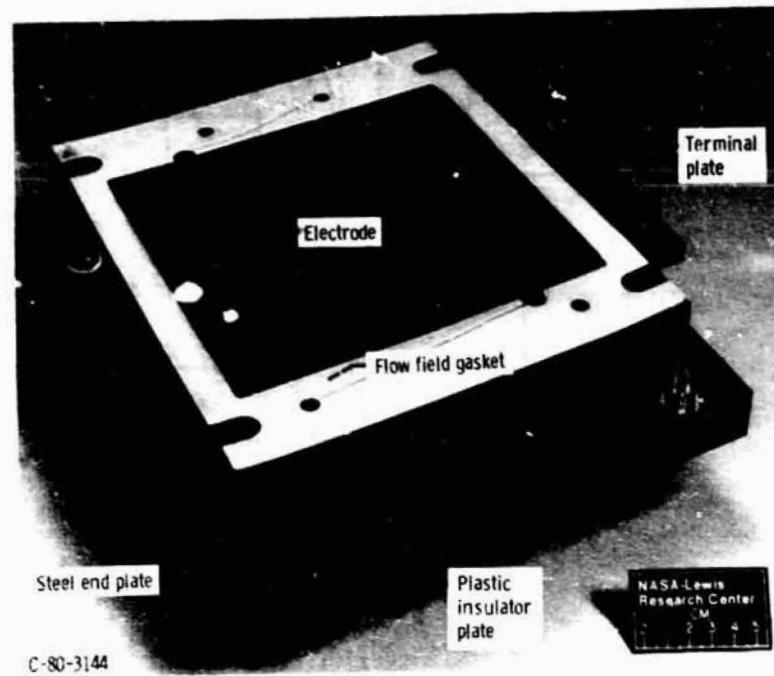


Figure 1. - Components of 310 cm² cell.

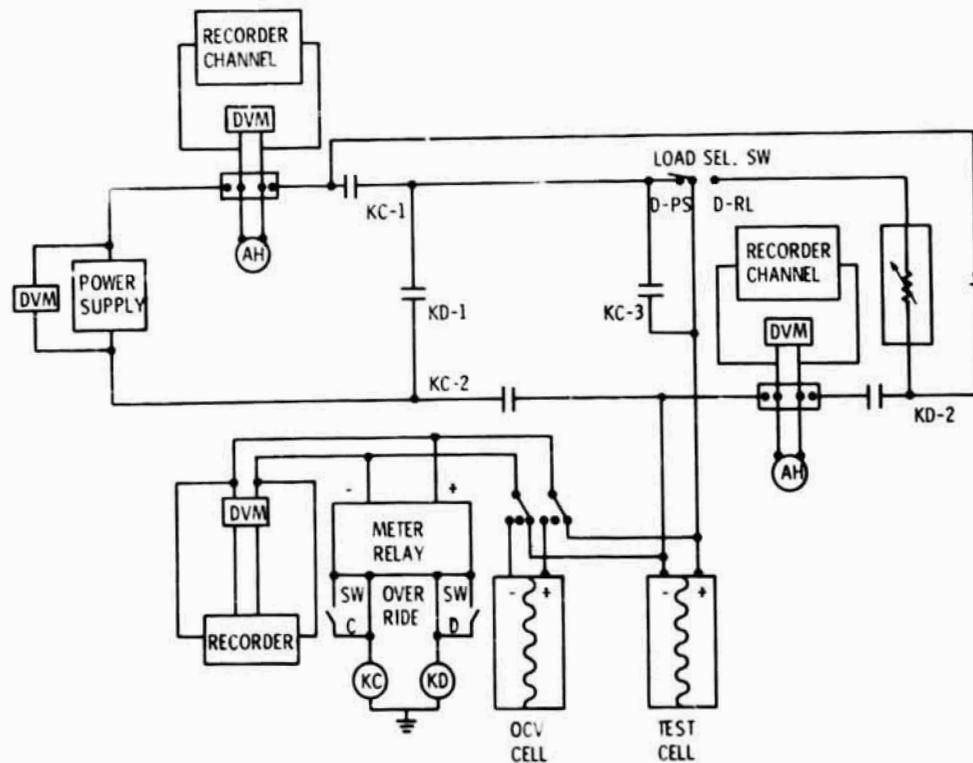


Figure 2. - Redox cell automatic cycling stand electrical diagram.

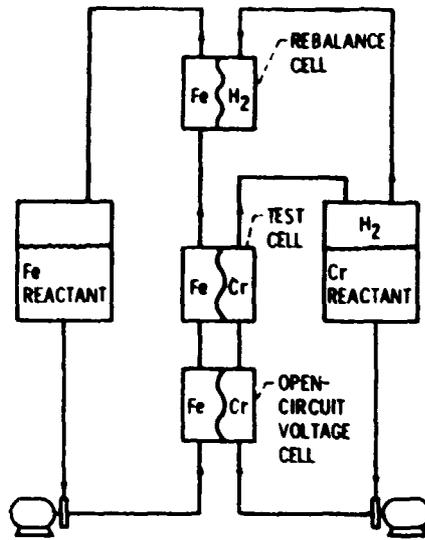


Figure 2A. - Redox cell automatic cycling stand hydraulic diagram.

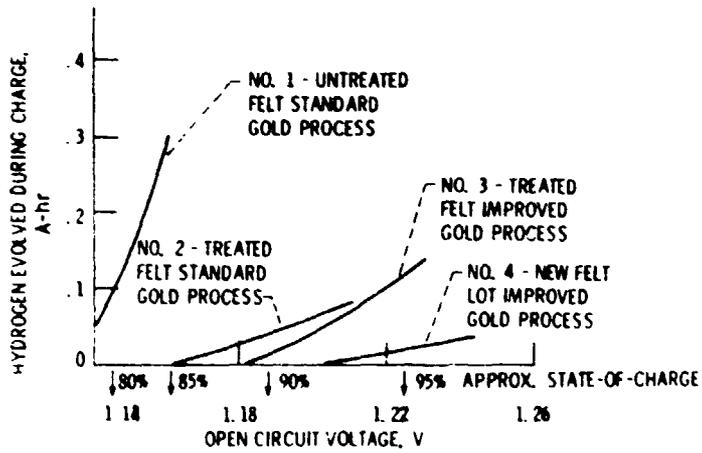


Figure 3. - Hydrogen evolution characteristics of

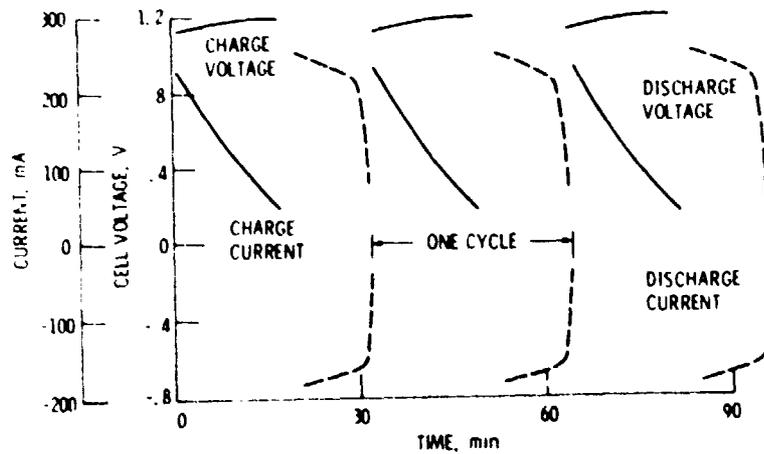


Figure 4. - Rapid cycle testing of new electrodes.

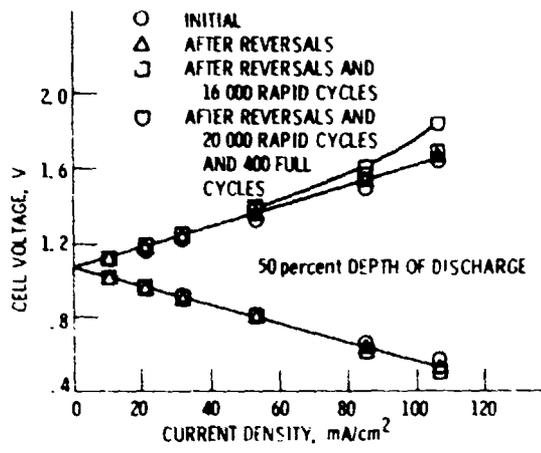


Figure 5. - Performance of 310 cm² single cell with new electrode before and after cell reversal studies and rapid cycling.

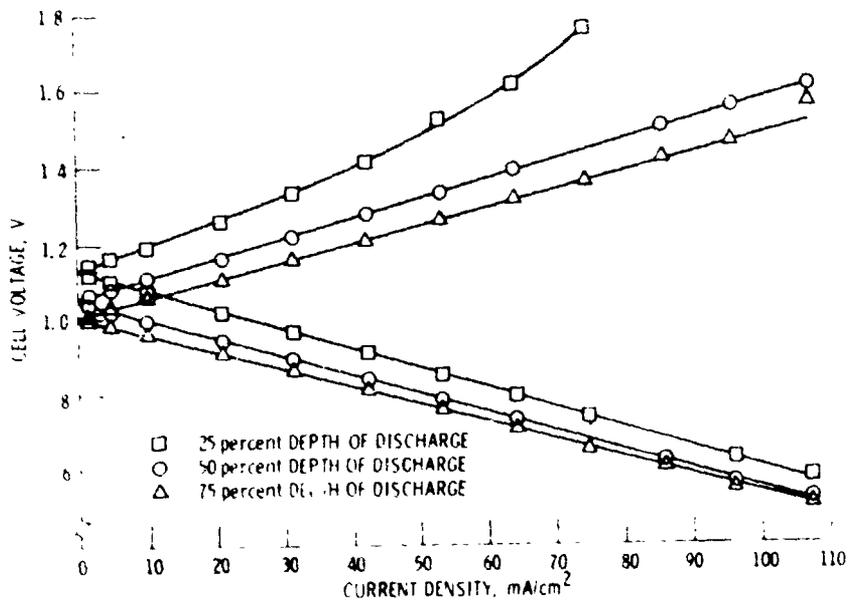


Figure 6. - Typical polarization characteristics for advanced chromium electrode for various states-of-charge

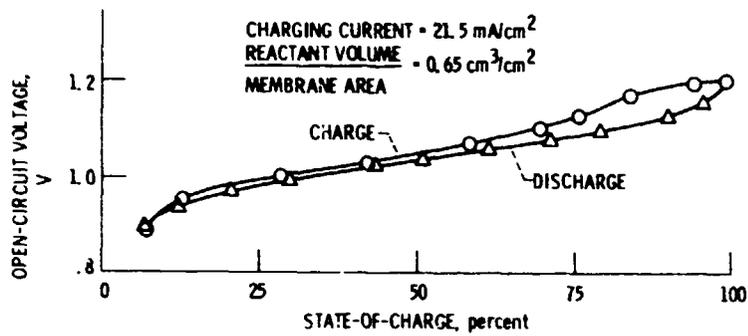


Figure 7. - Open-circuit voltage hysteresis of iron/chromium redox cell.

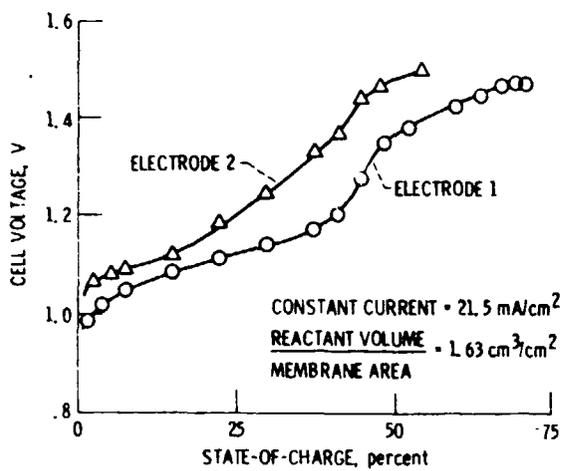


Figure 8. - Charging performance of redox cell as a function of chromium electrode preparation variations.

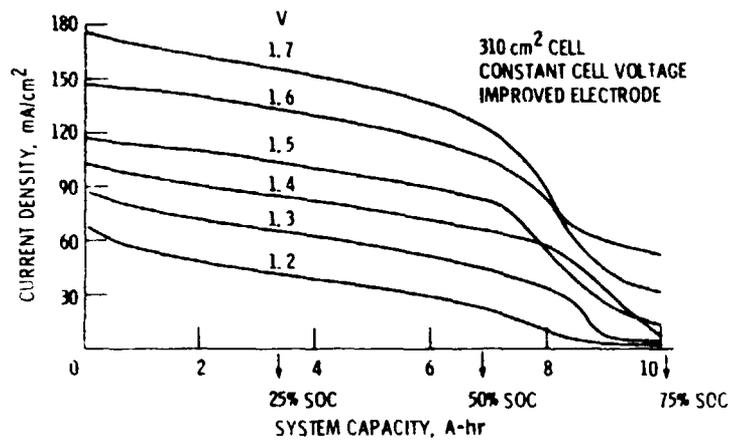


Figure 9. - Charge acceptance as a function of state-of-charge for various charge voltages.

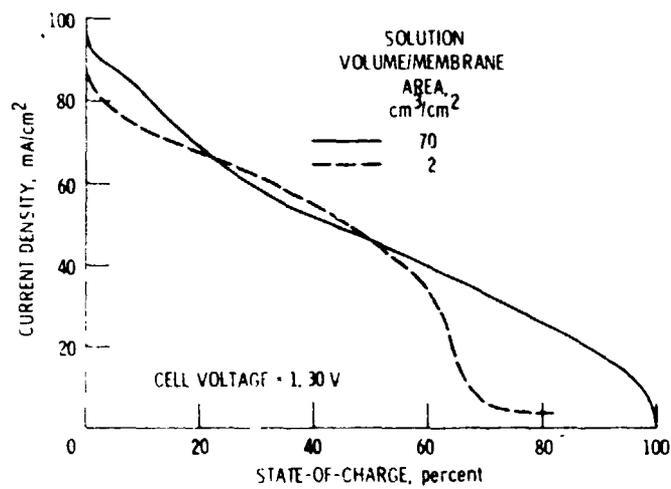


Figure 10. - Charge acceptance as a function of state-of-charge.

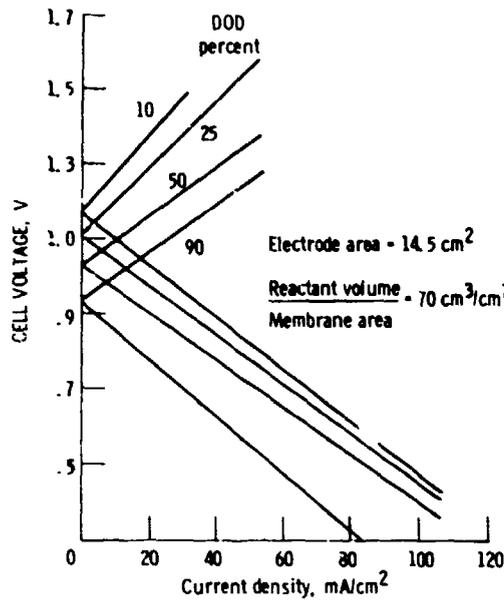


Figure 11. - Performance of a cell with large volume to area ratio.

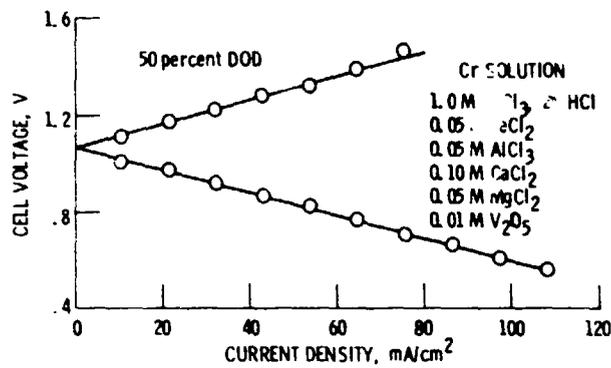


Figure 12. - Effect of chromium solution impurities on cell performance.

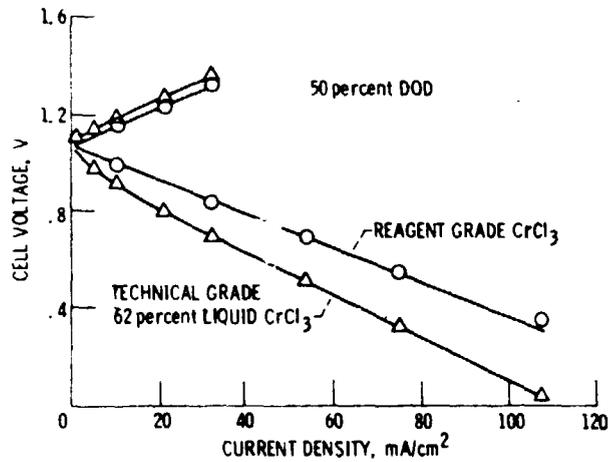


Figure 13. - Performance comparison of reagent grade and technical grade chromium chloride.