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August 1977

EXTENDED ABSTRACTS OF THE  
4TH BIENNIAL AIR FORCE  
ELECTROCHEMISTRY CONFERENCE

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EXTENDED ABSTRACTS OF THE 4TH BIENNIAL  
AIR FORCE ELECTROCHEMISTRY CONFERENCE

COMPILED BY:

Charles L. Hussey  
Lowell A. King

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August 1977

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Directorate of Chemical Sciences  
Frank J. Seiler Research Laboratory  
Air Force Systems Command  
US Air Force Academy, Colorado 80840

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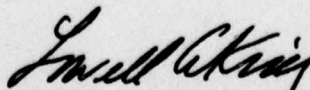
## FOREWORD

This report was prepared by the Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, CO.

The report presents extended abstracts of the presentations made at the 4th Biennial Air Force Electrochemistry Investigators Conference held at the United States Air Force Academy, 28-29 April 1977. Our appreciation is expressed to the authors, all of whom very kindly provided copies of their papers and/or abstracts for publication in this report.

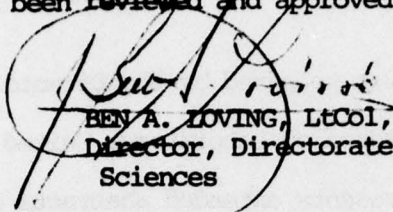
The Biennial Air Force Electrochemistry Investigators Conferences are jointly sponsored by Air Force Aero Propulsion Laboratory, the Air Force Office of Scientific Research, and the Frank J. Seiler Research Laboratory. They provide a forum for the discussion of current electrochemical investigations being made under grants and contracts and in-house, in both basic research and exploratory development. All of the Air Force investigators in these categories are invited to participate by formally presenting their work. Representation from other government agencies is solicited by inviting observers from various laboratories. These people are given an opportunity to formally present their programs if they wish to do so.

One of the key reasons for the existence of these conferences is to foster a mutual exchange of goals, approaches, and problems between the basic research and exploratory development communities within the total Air Force electrochemistry program. This exchange appears to be active and productive.



LOWELL A. KING, LtCol, USAF  
Senior Scientist

This technical report has been reviewed and approved.



BEN A. LOVING, LtCol, USAF  
Director, Directorate of Chemical  
Sciences

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## AIR FORCE BATTERY APPLICATIONS

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The Air Force's need for batteries is widely varied as can be seen from the matrix shown in figure 1. The uses range from small pieces of hand held survival equipment to large standby power systems for missile silos. In between these extremes lie all kinds of requirements for on board power for flight vehicles and prime power for weapons such as rockets and bombs. The number of battery types is also widely varied to meet the special requirements of each of the applications. The "X's" in the matrix denote a current use. The "O's" denote a planned use for which development is in progress or a potential use for which the technology is a candidate. Several of the applications do have common requirements and/or characteristics. These applications are grouped in the following discussion.

The aircraft and remotely piloted vehicle (RPV) or drone applications are somewhat related since the batteries see virtually the same environments and the uses in some cases are very similar. The uses for batteries aboard aircraft include: engine starting, either main engine, jet fuel starter, or auxiliary power unit; emergency power in the event of total electrical power loss; no break power for items such as inertial platforms, computers, and other parts of the flight control/guidance system; crash position locators. The RPV uses are mainly sources of power for recovery after engine shut off. The above uses are generally moderate drain applications but reliability and low temperature operation are a must. The cranking requirement is a severe electrical load and operation at low temperature is required.



The battery types presently used aboard aircraft and RPV's are vented lead acid, vented and sealed nickel cadmium, and vented silver zinc. The vented nickel cadmium is presently the most widely used due to its good high rate and low temperature performance, reasonable cost, and long life. Vented lead acid are used on some older aircraft and vented silver zinc batteries have been used in at least 2 fighter applications where weight is critical. The use of sealed nickel cadmium batteries have been limited to crash position indicators and avionics systems to date. RPV batteries are of the vented lead acid and silver zinc type. As can be seen from figure 1 other types such as: nickel zinc, nickel hydrogen, sealed nickel cadmium, and sealed lead acid show promise for use in the future.

The problem of engine cranking at low temperature remains and no good approach to the solution is in sight. The batteries require frequent maintenance, every 1 to 2 months, and as a result are relatively high life cycle cost items.

The spacecraft and satellite applications are grouped because they are very similar in the need for extremely high reliability, long life, lightweight, and similar operating environments.

The requirements aboard these vehicles range from those of a primary power source to power during eclipse and peak load power. The spacecraft requirements are generally those of a primary power source with high reliability and lightweight for periods of up to 90 days and large silver zinc primary or partially rechargeable batteries along with sealed rechargeable nickel cadmium batteries have generally been used. There have been some exceptions but are not discussed here. From figure 1 it is also evident that the metal gas and lithium batteries are candidates for future use. The satellite requirements can be generally broken into two classes, low earth and synchronous orbit. Both classes require

minimum weight and high reliability. The classes differ in that low earth orbit requires a large number of charge/discharge cycles and a relatively short calendar life. The synchronous orbit applications require long calendar lives and a relatively few charge/discharge cycles. With few exceptions, the sealed nickel cadmium batteries have been used for satellite applications to date. Figure 1 shows that nickel hydrogen will be a candidate in the future. Silver hydrogen may find use in some special situations and sealed lead acid batteries offer potential for a very low cost, limited life battery for situations where its weight can be tolerated.

The areas requiring further research and development for these applications are: increased cycle and calendar life; reductions in weight; and improvement in energy efficiency for rechargeable systems because of its impact on charging source (solar array) size in low earth orbit.

The next grouping of similar requirements is that of aircraft carried missiles, weapons, and expendable electronic countermeasure devices (ECM). In virtually all of these applications the battery is used as the primary source of power and must operate at low temperature after a long period of storage. Volumes are usually restricted and a reliable, low cost battery is necessary.

There have been many different kinds of batteries used in these applications; however, the missile and ECM devices have used reserve silver zinc and thermal batteries. Some weapons have used these batteries too, primarily thermals; however, many fuzing applications have used mercury, Le Clanche, lead fluoroboric acid, ammonia, and lithium batteries with the mercury and Le Clanche being the most popular. Improved thermal

batteries, reserve lithium, and perhaps reserve nickel zinc batteries are expected to find increased use in future applications of this type.

The intercontinental ballistic missile system battery requirements are somewhat unique. There are two general uses excluding the warhead which was covered under weapons. These requirements do not need low temperature operations but are more concerned with high reliability, radiation hardness (particularly on board equipment), long periods of standby operation, and minimum volume. The on board batteries are also required to be lightweight. The on board batteries are currently reserve silver-zinc type; however, reserve lithium type may be available for future use. The warheads use primarily thermal batteries. The missile silo batteries provide standby and emergency power capability. Vented lead acid batteries are presently used; however, future use of lithium primary and/or lithium primary/rechargeable nickel cadmium or nickel zinc or nickel hydrogen hybrid systems may occur.

Future needs are for smaller and lighter on board batteries. For silo use larger energy content in the existing volume and long life are needed.

The life support equipment requirements span a wide spectrum of needs for rescue equipment, such as radios and lights; chemical and biological warfare protective equipment; and protective clothing for needs such as high altitude ejection. The applications require low temperature operation, long storage or shelf lives, and minimum volume. Weight is a consideration but usually not a primary restriction.

The batteries used to date have been primarily the zinc-mercuric oxide type for radios and lights, with a few of the lithium-sulfur dioxide type; however, this is expected to be virtually all lithium in the future. Some of the chemical and biological warfare equipment



has used sealed nickel cadmium batteries; however, the future may see the use of sealed lead acid as a low cost option or nickel hydrogen batteries.

The main areas for future effort are extension of shelf and operating life, reduction of cost, and improvement of operation at low temperature.

PROPERTY	LEAD ACID	NICKEL CADMIUM	NICKEL HYDROGEN
SHelf life	1-2 years	1-2 years	1-2 years
Operating life	1-2 years	1-2 years	1-2 years
Cost	Low	Medium	High
Low temperature operation	Poor	Good	Excellent
Self discharge	High	Medium	Low
Recycling	Good	Good	Good
Weight	High	Medium	Low
Volume	High	Medium	Low
Temperature range	0 to 30°C	-20 to 50°C	-40 to 60°C
Operating voltage	2.1V	1.2V	1.2V
Charging voltage	2.4V	1.4V	1.4V
Charging current	0.1C	0.1C	0.1C
Discharging current	0.1C	0.1C	0.1C
Depth of discharge	50%	80%	80%
Number of cycles	100	500	1000
Energy density	30 Wh/kg	60 Wh/kg	100 Wh/kg
Power density	200 W/kg	200 W/kg	200 W/kg
Efficiency	80%	85%	90%
Environmental impact	High	Medium	Low
Availability	High	Medium	Low
Reliability	High	Medium	High
Maintenance	High	Low	Low
Safety	High	Medium	Medium
Design flexibility	High	Medium	Low
Manufacturing complexity	Low	Medium	High
Material availability	High	Medium	Low
Recycling technology	Advanced	Advanced	Advanced
Research and development cost	Low	Medium	High
Commercial maturity	High	Medium	Low
Government support	High	Medium	High
Industry support	High	Medium	Low
Academic support	High	Medium	High
Overall rating	Good	Very Good	Excellent

	VENTED Pb ACID	SEALED Pb ACID	VENTED Ni-Cd	SEALED Ni-Cd	RECHG. Ni-Zn	PRI Ni-Zn	RESERVE Ag-Zn	PRI. Ag-Zn	RECHG Ag-Zn	Ni-H <sub>2</sub>	Ag-H <sub>2</sub>	LI-SO <sub>2</sub>	LI-SOCl <sub>2</sub>	LI-SO <sub>2</sub> Ca <sub>2</sub>	H <sub>2</sub> O-ZN	TERMINALS	Ca-CdCd <sub>2</sub> Mg-V <sub>2</sub> O <sub>5</sub>	LI-MoCl <sub>5</sub>
AIRCRAFT	X	0	X	0	0				X	0								
SPACECRAFT				X				X		0	0	0	0	0				
SATELLITES		0		X						0	0							
MISSILES (A/A & A/G)						0	X					0	0				X	0
MISSILES (ICBM)	X			0	0	0	X					0	0	0				
RPV	X	0	X	X	0				X			0	0					
WEAPONS						0	X					0	0	0	X	X	X	0
LIFE SUPPORT		0		X						0		0	0	0	X			0
ECM						0	X					0	0	0			X	0
MISCELLANEOUS	X	0	X	X	0					0		0	0	0	X			

FIGURE 1

IN-HOUSE RESEARCH AT AFAPL

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In-house research at the Air Force Aero Propulsion Laboratory (AFAPL) is divided into three different tasks. Two of these are exploratory development types and the other, which has been newly formed, is concerned with battery electrochemistry research. In exploratory development in-house testing of new battery types, such as nickel hydrogen and silver hydrogen, fabrication of nickel hydrogen-cadmium battery electrodes, and development of accelerated test procedures for nickel cadmium batteries are being pursued. In the newly formed electrochemistry task investigations of nonaqueous couples, such as  $\text{Li}/\text{SOCl}_2$ , state-of-charge indication in Ni-Cd cells, electrocatalysis, and solid electrolytes are underway. Work in the electrochemistry task is supported by the Air Force Office of Scientific Research and performed by AFAPL scientists and engineers.



COORDINATED NASA/AF NICKEL-CADMIUM BATTERY TECHNOLOGY PROGRAM

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This presentation describes the NASA/AF nickel-cadmium (Ni-Cd) battery technology program which is being coordinated by JPL to provide spacecraft missions in the 1980's with lighter and/or longer lived Ni-Cd batteries for low earth orbit, geosynchronous orbit and planetary missions. The goal is to double the energy density and/or life of the system. The relationship of life and energy density based on depth of discharge and type of mission is discussed. The failure modes and mechanisms are discussed to point out the critical design variables which effect Ni-Cd cell life. Cell component weights are listed, approaches for reducing weight are discussed, and program tasks by each organization are described. Progress has been made in weight reduction, understanding of life/reliability mechanisms and development of a process for manufacturing more stable electrodes. An accelerated and predictive life test program is approximately 50% complete. A comprehensive literature search with abstracts and index was published. A treatise on the cadmium electrode was published. Major problem areas which require more effort are positive-to-negative material ratio, negative precharge level, inter-electrode spacing and compression, effects of impurities and additives, a more stable separator and optimization of electrodes for thickness, porosity and loading levels.

## NICKEL-HYDROGEN BATTERY PROGRAMS

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A description of the operation and characteristics of the nickel-hydrogen cell and of the results of Air Force Aero Propulsion Laboratory and Hughes Internal Research and Development programs was given. Brief descriptions of the components of the battery, electrode reactions, advantages over nickel-cadmium, and applications to satellites were made. Components of the cell included positive and negative electrodes, separators, case and stack support mechanical components. Stack designs included both the state-of-the-art back-to-back and recirculating oxygen design using a wick electrolyte return. The materials and processes used to manufacture electrodes, the operation of the electrodes during normal charge and discharge as well as overcharge, and the structure of both the positive and negative electrodes were discussed. The functions and requirements of the separator for both gas permeable and impermeable types include such critical items as electrical insulation, ionic conductivity, heat and chemical resistance, wettability and the ability to act as a reservoir during cycling. The generation of oxygen during overcharge and its recombination are critical to the operation of the cell and are greatly influenced by the separator. Electrolyte loss mechanisms which were found to be most important were displacement and vapor transfer. Brief descriptions of the Air Force programs, under which a large portion of this work was done, included the Nickel-Hydrogen Exploratory Development Program, Failure Mechanisms Study, and Advanced Development Program.

## NICKEL-ZINC BATTERY FOR AIRCRAFT AND MISSILE APPLICATIONS

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Interim results are presented for a program to develop nickel-zinc batteries for aircraft and missile applications. For aircraft applications, a nickel-zinc battery has been developed to compare to the MS-24497-5 nickel-cadmium aircraft battery. The nickel-zinc battery is the same size and nominal voltage as the nickel-cadmium battery, but delivers 40 ampere-hours as compared to the nickel-cadmium capacity of 22 ampere-hours. Scaled experimental nickel-zinc cells have achieved 400 cycles under a discharge regime equivalent to an aircraft battery delivering rated capacity at the one hour rate. Simulated aircraft starting has been performed at temperatures down to  $-20^{\circ}\text{F}$ .

For missile applications, a remotely activated nickel-zinc battery has been developed to compare to the remotely activated silver-zinc battery. The nickel-zinc system was chosen for this study because of its superior wet stand capability, superior low temperature performance, higher operating voltage and lower cost. The configuration studied for both batteries was the Falcon missile battery. By utilizing the superior wet stand capability of the nickel-zinc system, a battery was designed with a significantly greater ratio of active material to separator. This feature resulted in the nickel-zinc battery exceeding the delivered capacity of the silver-zinc battery. The silver-zinc battery delivers 1.6 ampere-hours at 13.9 volts under a 32 amp load, while the nickel-zinc battery delivers 2.0 ampere-hours at 14.7 volts under a 32 amp load. Costs for the silver-zinc battery are \$12.46/watt-hour, while the nickel-zinc costs are projected at \$7.52/watt-hour.



## SILVER HYDROGEN ENERGY STORAGE

G. L. Holleck  
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55 Chapel Street, Newton, Mass. 02158

EIC Corporation is presently conducting an investigation of Ag/H<sub>2</sub> cells to determine the feasibility of achieving 35 Whr/lb, 500 deep cycles and one year life. This includes the following major program tasks: (1) evaluate Ag/H<sub>2</sub> cell performance, (2) determine failure mechanisms, (3) find solutions to problem areas, (4) develop a mathematical model for rolled Ag/H<sub>2</sub> cells and (5) build prototype 50 Ah Ag/H<sub>2</sub> cells.

The Ag/H<sub>2</sub> system uses the strong electrode of the Ag/Zn battery and the H<sub>2</sub>/O<sub>2</sub> fuel cell. While this eliminates the problems of the Zn and O<sub>2</sub> electrodes, it retains the difficulties associated with the relatively high solubility of Ag<sub>2</sub>O in the KOH electrolyte. Especially attractive features of the Ag/H<sub>2</sub> system include its high energy and power density and its insensitivity to overcharge, overdischarge and cell reversal.

Main problem areas which have to be addressed are: (1) Ag migration, (2) electrolyte management, (3) oxygen management and (4) heat dissipation.

Restriction of soluble Ag<sub>2</sub>O to the cathode side of the cell requires the use of argentostatic membranes similar to those presently used in Ag/Zn cells. Membrane stability and short circuits caused by silver bridging are the main difficulties. These membranes also impact strongly on electrolyte management. In addition to overall changes in electrolyte concentration and volume, the variations in the cathode and anode half cells have to be considered separately. They are linked together by the various transport processes (diffusion, electromigration and hydrostatic flow) in the barrier layers.

On overcharge, oxygen is generated at the silver electrode which has to recombine with hydrogen at the anode. Safety considerations mandate low oxygen concentrations in the cell gas at all times: This requires careful consideration of mass transport (O<sub>2</sub> diffusion) in the cell gas and high reaction rate at the hydrogen electrode.

Good thermal management has to ensure small temperature differentials (a few degrees C) between cell stack and cell case to avoid water loss from the stack via an evaporation-condensation mechanism.

Experimental evaluation of important design variables using a mathematical test matrix is presently in progress.

This effort is supported by the U.S. Air Force, Air Force Systems Command, Aeronautical Systems Division, Wright-Patterson Air Force Base under Contract No. F33615-76-C-2093.

## RESEARCH ON NEW CATALYSTS AND ELECTROLYTES FOR ADVANCED FUEL CELLS

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The Army has had an active fuel cell effort since the late 1950's. During this extended period almost all the major technologies have been examined for their potential applicability to the Army mission of mobile field power generation. These have ranged from those based on caustic electrolytes thru acidic, phosphoric and sulfuric, to molten carbonates. The major goal of the Army fuel cell program, at present, is the development of a family of silent, lightweight and efficient electric power sources in the power range of 500 watts to 5 kilowatts. The selected technology for this development program is an air cooled phosphoric acid fuel cell using hydrogen supplied either by steam reforming of methanol or by thermocatalytic cracking of logistic fuels (JP-4, diesel or gasoline).

This system development program is supported by well balanced fundamental research efforts in the areas of electrocatalysis, electrolytes, and electrochemical reaction mechanism and reaction kinetics. The goals of this research program are to increase the basic understanding of fuel cell processes and electrode reactions, and to promote with this the development of less expensive and more efficient fuel cells.

The research in electrocatalysis is pursued in two directions, by modification and better utilization of the presently used platinum catalyst and by substitution of this noble metal by alloys and compounds with electronic surface properties similar to platinum. The experimental techniques employed for these investigations include conventional electrochemical methods and surface research techniques such as low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED), Auger electron spectroscopy (AES) and residual gas analysis (RGA) by mass spectrometry. This research resulted in the elucidation of the reaction mechanisms of hydrogen-carbon monoxide mixtures on platinum partially covered with sulfur, the determination of catalyst-substrate interactions of carbon supported platinum electrocatalysts, and the analysis of the surface composition of electrocatalytic active tungsten carbide.

The research on the electrochemical activities of electrolytes for fuel cells has the objective to search for new fuel cell electrolytes with physical chemical properties superior to phosphoric acid. Physical chemical properties such as vapor pressures, conductivities, viscosities, gas solubilities, and anion adsorption are being determined for promising



electrolytes. The results in this program have demonstrated the great beneficial effect which electrolytes can have on fuel cell performance. Trifluoromethanesulfonic acid monohydrate proved to be superior to phosphoric acid in the electrochemical oxidation of propane and hydrogen and the reduction of oxygen under comparable conditions. A further advantage of this novel electrolyte is that it apparently increases the carbon monoxide tolerance of the fuel cell which allows the utilization of rather impure fuels. However, Trifluoromethanesulfonic acid monohydrate has also physical chemical properties such as a relatively high vapor pressure and wetting characteristics which are not optimal for fuel cell applications. Therefore, the search for new electrolytes with superior properties will be continued.

Rotating ring and disk electrode studies are being combined with mass spectrometric and gas chromatographic investigations for the elucidation of the mechanisms and kinetics of fuel cell reactions. The first result in the accurate definition of processes occurring at the electrode/electrolyte interface whereas the latter permit the analysis of reaction products and the establishment of the reaction kinetics. Results of these investigations elucidated the adsorption mechanisms of several structurally different compounds (propane, benzene, and ethylene), and the subsequent desorption of the products formed on the electrode surface during various stages of electrooxidation.

We hope that these research efforts will not only support the development of less expensive and more efficient fuel cells for the Army, but also contribute considerably to the success of the National Fuel Cell Program.

## LITHIUM INORGANIC ELECTROLYTE BATTERY INVESTIGATIONS

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In accordance with requirements of Air Force Contract No. F33615-74-C-2071, Honeywell Power Sources Center designed, fabricated, and tested hardware versions of the lithium-thionyl chloride battery system. Batteries for three potential operational uses were investigated in an effort to evaluate their performance capabilities for meeting optimum requirements for life support and spacecraft applications.

Goals embodying the desired performance of lithium inorganic electrolyte oxychloride batteries for future and conceptual equipment were defined in the Statement of Work as targets for the tasks specified.

The state of the art at the start of the project was embodied in the first series of Life Support Cells, built on the basis of previous experience with this technology at Honeywell and investigation into the literature. Two later series of Life Support Cells and two series each of the two different types of Spacecraft cells were built and tested on the basis of an analysis of the baseline series and ongoing cell improvement studies.

Recognizing the highly reactive chemistry of the cells, Honeywell performed tests on the larger Spacecraft cells at their ordnance testing ground and devised a scheme for remote activation. Safety testing beyond that required by the project was carried out, which justified the care exercised in handling the Spacecraft cells.

The most severe problem encountered with the baseline series of cells was polarization of the lithium anode due to a severely passivating film. Dramatic improvement was effected by the addition of 5 percent by weight of  $SO_2$  to the electrolyte solution.

By testing hardware models of cells and conducting cell improvement studies, Honeywell's efforts during this project significantly advanced the state of the art of this technology as it applies to Life Support and Spacecraft functions. Pertinent experimental and cell performance data were presented.

Achievements versus the energy density goals were as follows:

Cell Type	Energy Density			
	Goal		Achieved	
	WH/lb	WH/in <sup>3</sup>	WH/lb	WH/in <sup>3</sup>
Life Support	120	18	155	13.5
Spacecraft "A"	175	15	175	13.1
Spacecraft "B"	350	25	262	17.2

Recommendations for further experiments in the areas of safety and long term storage were presented.



POLARIZATION CHARACTERISTICS OF Ca/CaCrO<sub>4</sub> THERMAL CELLS

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A factorial experiment was conducted in which single cells of the Ca/LiCl-KCl-SiO<sub>2</sub>/CaCrO<sub>4</sub>-Fe system, having a Ag/AgCl reference electrode in them, were discharged at constant current. Three factors were investigated: temperature, current density, and composition of the Depolarizer-Electrolyte-Binder pellet. An analysis of variance was performed on the data using a CDC 6600 computer.

It was found that the linear drop in voltage occurring during the plateau portion of the discharge is due primarily to IR free polarization at the cathode. This polarization is caused by a chemical reaction in which the Li<sup>+</sup> ions in the electrolyte take part. End of life is caused by the buildup of a resistive layer at the anode. This layer blocks the anode prior to the cell utilizing all of its active materials.

Several two-way interactions were noted which give an insight into the behavior of these thermal cells during discharge and are useful in the design of batteries for specific applications.

## THERMAL BATTERY LIMITATIONS

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Historically, thermal batteries have been noted for high current density with very short lives. The present long life batteries have advanced to fifty minutes with a current density of  $30 \text{ ma/cm}^2$ . Work being performed on the Wright Patterson Air Force contract is aimed at extending present limits to achieve a thirty minute thermal battery with a current density of  $180 \text{ ma/cm}^2$ . Volume, weight and current density goals of the program are four to six times above the present levels of thermal batteries.

Establishment of weight and volume priorities on present long-life batteries show that the container/header and insulation are the most likely areas for reductions necessary to meet the goals. The present coulombic efficiencies for the  $\text{Ca/CaCrO}_4$  system is 20% to 30% for the cathode. The goals of this program have been set at 75% for both anode and cathode with 60% to 70% having been demonstrated on single cell tests using a  $\text{LiAl/CaCrO}_4$  system. Investigative areas into increasing anode efficiencies have included the filling of honeycomb structures with powdered calcium and lithium aluminum and the vacuum deposition of calcium onto honeycomb and expanded metal. The addition of electrically conductive particles and the substitution of various structures for collector plates have been used in arriving at an improved cathode efficiency.

## NEW HEAT SOURCE COMPOSITION FOR THERMAL BATTERIES

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Catalyst Research Corporation is presently engaged in a contract with the Air Force to develop a fast starting battery which uses an iron powder/potassium perchlorate mixture as the primary heat source. In our design, the use of Type II zirconium is limited to the fuze strip only, which means that production hazards and material availability problems can be reduced considerably.

The prototype batteries use a new thermal battery chemistry with a design tailored to meet the "Maverick" specifications. They are comprised of 3 inch diameter cells with fast burning iron based heat powder, molten metal anode, conventional lithium chloride-potassium chloride electrolyte, and a proprietary depolarizer. In previous designs this system was able to achieve current densities of greater than 12 amps/square inch, but start times were too long to meet these new specifications. The Maverick battery specifications require an operating temperature range of  $-65^{\circ}$  to  $+160^{\circ}\text{F}$  with a life of 105 seconds at a 4.2 amp constant load. Start requirements for the cold and hot units were .55 and .45 seconds, respectively.

The first step taken to improve start performance was to characterize and optimize the heat mixture. The pyrotechnic combination of iron and potassium perchlorate was first investigated in the late sixties and found to have several advantages over zirconium based heat paper. The iron powder serving as fuel and the potassium perchlorate as the oxidizer could be processed dry without danger of ignition and because of an excess of metal the ignition product was still conductive. Thus, the mixture could be pressed into mechanically strong pellets that served as intercell connectors for the battery after firing. Several types of iron powder were investigated and two were selected for their good chemical reactivity and handling properties. Blends of these two were also evaluated.

The burning rate and calorific output of this heat mixture are directly proportional to the ratio of fuel to oxidizer. The proportions selected for use in this battery were 86% iron and 14% perchlorate by weight.

Using this ratio, three blends of heat mixture were made with varying amounts of Type II iron (the most chemically reactive). From these results, the mixture with the most promise appeared to be Blend #3, which has a fast burning rate and good ignition sensitivity even at high forming pressures. The ignition sensitivity of this mixture corresponds to a 10 fold decrease however, when compared to zirconium based heat paper.

The second important factor controlling the start time of a thermal battery is the mass of the cell itself. The energy released from the heat source must raise the temperature of the cell to its operating temperature of approximately  $500^{\circ}\text{C}$  in a fraction of a second to meet performance requirements.



Initiation of a thermal battery happens in three basic steps. Ignition occurs when a primer or electric match is fired by an external source. The reaction is essentially immediate. The blast from the match ignites the zirconium/barium chromate fuze strip which constitutes the second step. The burning rate of the fuze strip is dependent on composition as well as placement of the strip. The third and rate limiting step of battery initiation is the burning of individual heat pellets. Typically, this is found to be in the range of .25 to .75 seconds for a three inch pellet. There is also a delay associated with heat transfer into the rest of the cell, particularly the electrolyte layer which must become molten before the cell can function. This delay accounts for the difference between pellet burning time and battery start time.

Near the end of Phase I of our program, the Maverick battery prototypes were meeting specification, and attention was turned to the newly proposed imaging infrared (IIR) missile design. The battery needed for this application was similar, but with higher output.

In conjunction with our contract representative, we proposed a change in the scope of the development program which allowed us to develop our prototype to meet this new specification. Presently we are testing our prototypes to the new specifications and will finalize the design once Phase II testing is complete.

We have shown with this program that fast-starting (under .5 seconds) batteries are indeed possible using an iron-based heat source and are consistent and reliable in performance. The benefits gained by using this heat mixture are safety, ease of handling, and a large, reliable domestic source of raw material.

## IMPROVED THERMAL BATTERY

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KDI SCORE has been awarded a 30 month program by Wright-Patterson Air Force Base to develop a 28 volt, 30 ampere battery to last for 30 minutes, using Ca/LiCl-KCl/CaCrO<sub>4</sub> system, and to operate in temperature range of -54°C to +71°C. If developed, this could replace Silver-Zinc batteries in some applications. Only batteries utilizing Sandia Technology have exhibited satisfactory "thermal" life (4140 seconds). Considerable improvement is needed (in the existing state-of-the-art) in the area of increasing electrical capacity at higher current densities.

The program is built around the following decision points: Literature Survey, Physical and Chemical Analysis of Material Properties, Thermal Characteristics of Chemical Mixes, Single Cell Testing, and Battery Testing.

The following conclusions were drawn from the results of single cell tests and battery tests:

1. A definite correspondence was established between results observed in battery tests and single cell tests.
2. Increased pressure improved life up to a certain level and also lowered start time of the batteries.
3. Change in inert material content changed the performance of the systems. Increased amount of inert material improved performance at low current density and vice-versa.
4. Different systems are required for optimum performance at different current densities.
5. Homogeneous DEB pellets were good at low (50 ma/cm<sup>2</sup>) and medium (95 ma/cm<sup>2</sup>) current densities, but two layer pellets were good at high current densities (350 ma/cm<sup>2</sup>).
6. Additives to Ca/CaCrO<sub>4</sub> system could change the voltage on load to over 3.0 volts per cell and at the same time improve start time. But higher peak need not extend the life.

It is, however, felt that more basic research is needed in the following areas for Ca/KCl-LiCl/CaCrO<sub>4</sub> system to provide a better understanding of the reaction mechanism in the batteries:

1. The film formed on calcium in storage, its composition and role in internal reactions.
2. The reason for difference in performance of strip calcium and vacuum deposited calcium.
3. Reaction rates and mechanism involved in CaLi<sub>2</sub> alloy formation at various current densities.
4. Formation of double salt KCaCl<sub>3</sub> and other products of reaction.
5. Interactions involving Ca, KCl-LiCl, CaCrO<sub>4</sub>, cab-o-sil, with respect to internal heat generation at different current densities.
6. In-depth study of the solubility of CaCrO<sub>4</sub> in KCl-LiCl eutectic.

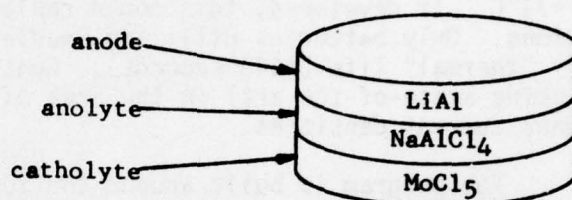
## DEVELOPMENT OF THE ALUMINUM CHLORINE BATTERY

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The Eureka Advance Science Corporation has manufactured a new thermal battery. This battery was constructed of three layer pelletized thermal cells like those shown in Figure 1.

An aluminum  
chlorine cell

Figure 1



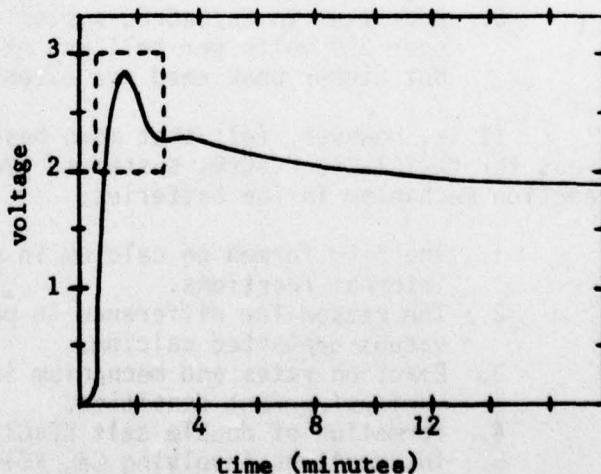
The anode is a lithium aluminum alloy. The best alloy used was 28 w/o lithium. The cathode is  $\text{MoCl}_5$  mixed into a matrix of graphite and  $\text{NaAlCl}_4$ . The anolyte layer, the separator layer, is  $\text{NaAlCl}_4$  mixed with Cab-O-Sil to prevent flow of the molten salt.

This cell was developed at Frank J. Seiler Research Laboratory at the Air Force Academy. Eureka was contracted to try to construct a battery from these cells and having accomplished that, develop the battery to a useful product.

Before any attempt to make batteries was made, 135 single cells were made and tested. Figure 2 is a typical discharge curve for a single cell test.

A typical discharge curve  
for an aluminum chlorine  
single cell test

Figure 2





One immediately obvious feature of this curve is the area in the dotted box. This high voltage peak was originally thought to be a random phenomenon. This voltage peak was responsible for a first impression that the peak voltage of the cell was not very reproducible.

A factorial design study done on four variables of the cell showed that the high voltage peak was not a random phenomenon but was in fact related to the make up of the cell and the formula of the catholyte. The factorial design study also showed:

- (1) The peak voltage depended upon the catholyte formula and was independent of the cell make up.
- (2) The 80% lifetime was dependent upon the relative size of the anode and cathode and was relatively dependent of the catholyte formula.
- (3) The factors that influence the energy density are identical to the factors that influence the lifetime but are not at all similar to the factors that influence peak voltage.

The first discharge curve for an aluminum chlorine battery

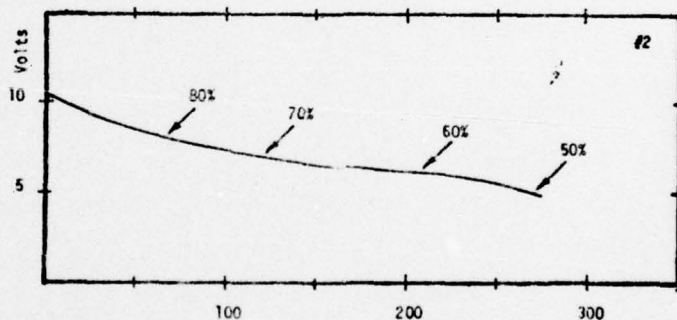


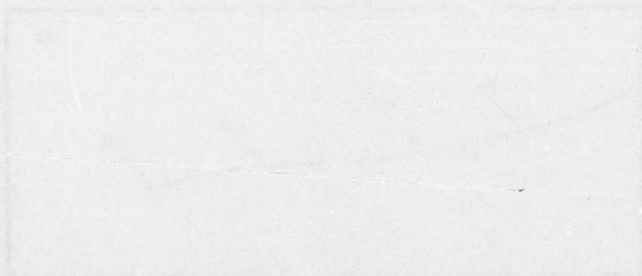
Figure 3

Figure 3 is the discharge curve for the first aluminum chlorine battery. The first battery tests were quite encouraging because the battery worked quite well. It did not vent, deform, or over heat, and the discharge curve was clean and free of electrical noise.

The calorie value of the heat paper used to make these batteries was optimized and by testing identical units at different test temperatures it was proven that the battery could function at a temperature range of at least  $-65^{\circ}\text{F}$  to  $+165^{\circ}\text{F}$ .

The conventional  $\text{Zr}/\text{BaCrO}_4$  heat pads were replaced by experimental  $\text{Fe}/\text{KClO}_4$  heat disks. The initial tests showed a dramatic 400 to 500% increase to 80% lifetime. Later tests displayed catastrophic complications between the iron heat source and the cell stack. Continued

experimentation resulted in a 28.8 volt battery which produced a current density of  $43.3 \text{ mA/cm}^2$  for six minutes, with a noise free trace. The operating battery was cool enough to hold in the bare hand.



## The Aluminum Chloride Thermal Battery Program

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The thermal battery research program at FJSRL is a 2.4 man year effort budgeted at \$80,800 for the period 1 July 1976 to 30 September 1977. The three main areas of current research are:

- a. The  $\text{LiAl}/\text{MoCl}_5$  Thermal Cell
- b. The  $\text{LiAl}/\text{CuCl}_2$  Thermal Cell
- c. A Cathode Screening Study

Work on the  $\text{MoCl}_5$  and  $\text{CuCl}_2$  cathodes is complete and will be discussed in more detail. The cathode screening study is in progress and will furnish the basic foundation for efforts in FY78.

Low temperature thermally activated reserve batteries (thermal batteries) were evaluated using single cell testing techniques (1). The electrochemical system under investigation utilizes LiAl alloy anodes, NaCl-saturated  $\text{AlCl}_3$  electrolytes, m.p.  $158^\circ\text{C}$ , and  $\text{CuCl}_2$  or  $\text{MoCl}_5$  cathodes. Single cells were operated at temperatures between  $175^\circ\text{C}$  and  $250^\circ\text{C}$ . This electrochemical system is a candidate to replace or complement current thermal battery systems operating at much higher temperatures (2). Previous work (2,3) in this laboratory identified copper(II) chloride and molybdenum(V) chloride as potentially excellent cathodes in the chloroaluminate electrolyte. The purpose of that work was to study these two cathodes with respect to the following variables:

- (a) graphite content, (b) alloy anode composition, (c) particle size,
- (d) anode/cathode-electrolyte ratios, (e) current density, and
- (f) temperature.



Trilayer single cells containing the anode, separator, and cathode were fabricated in a Carver die. Pressures used to compact the successively added layers were 16,700, 23,000, and 29,200 lb/in<sup>2</sup> for anode, separator, and cathode layers respectively. The cathode layer contained graphite as the current collector. Typical single cell compositions for the MoCl<sub>5</sub> and CuCl<sub>2</sub> cathodes are given in Table I.

Table I. Typical Compositions

A. For the LiAl/MoCl<sub>5</sub> Single Cell

Section	Wt (g)	Component
Anode	0.27	60.2 a/o LiAl
Separator	0.78	EB Mixture <sup>a</sup>
Cathode	{ 0.64	EB Mixture <sup>a</sup>
	{ 0.72	MoCl <sub>5</sub> (30-50 mesh)
	{ 0.23	Graphite (Fisher)

B. For the LiAl/CuCl<sub>2</sub> Single Cell

Anode	{ 0.50	60.2 a/o LiAl
	{ 0.50	EB Mixture <sup>a</sup>
Separator	0.90	EB Mixture <sup>a</sup>
Cathode	{ 0.45	EB Mixture <sup>a</sup>
	{ 0.50	CuCl <sub>2</sub> (50-100 mesh)
	{ 0.16	Graphite (Superior-purified)

<sup>a</sup>EB Mixture: Electrolyte (49.85 m/o AlCl<sub>3</sub>-50.15 m/o NaCl) + Binder (10 w/o Cab-O-Sil)

Differences in the composition of the single cells for the two cathodes are the result of two different approaches to the study of single cell performance. For the MoCl<sub>5</sub> cathode the aim was to arrive at an optimized composition that would yield the highest energy density to complete discharge from the cell. Fisher graphite was used because it was the graphite selected in the development of the LiAl/MoCl<sub>5</sub> thermal battery by the Eureka Advanced Science Corporation (4).

Utilization of the same graphite would allow direct comparison with their data. For the  $\text{CuCl}_2$  cathode our goal was to realize the effect of different commercially available active anode and cathode materials on single cell performance.

The study of the  $\text{MoCl}_5$  cathode (3) showed that the optimum energy density was obtained using the 60.2 a/o LiAl alloy, a 30-50 mesh  $\text{MoCl}_5$  particle size, 0.23 g graphite in the cathode, and the anode/cathode/electrolyte quantities depicted in Table IA. The optimal single cell configuration delivered 38 W-Hr/lb to zero volts at a discharge rate of  $15 \text{ mA/cm}^2$  at  $175^\circ\text{C}$ .

A method for the analysis of discharge data previously developed by Balewski and Brenet (5) for the analysis of Leclanche batteries was applied to thermal battery single cell test data. This procedure requires a plot of the slope of the discharge curve,  $dQ/dV$ , versus the average voltage,  $\bar{V}$ . For  $\text{MoCl}_5$  single cells using Fisher graphite at operating temperatures of  $175$ - $275^\circ\text{C}$ , such plots show as many as six separate discharge peaks. The major peaks in the discharge reaction shift to lower potentials with increasing operating temperatures. Previous studies by Phillips and Osteryoung (6) had indicated that there were only three discharge steps at  $175^\circ\text{C}$  for  $\text{MoCl}_5$ . To reconcile the test data additional experiments utilizing a purified Superior graphite (7) were accomplished. These new data confirmed that there were only three peaks in the discharge curve for  $\text{MoCl}_5$  and that the additional peaks were due to trace iron impurities in the Fisher graphite. The presence of iron was further confirmed by x-ray analysis. The purified graphite samples also confirmed the fall off in cell

performance due to increasing temperature. We feel that the decreased performance at higher temperatures is due to the low melting and boiling point of the  $\text{MoCl}_5$ : 195°C and 268°C, respectively (8). This may limit the application of the  $\text{MoCl}_5$  thermal battery to the temperature region between 175°C and 250°C, since ignition of present heat sources in the  $\text{MoCl}_5$  thermal battery has shown momentary temperatures in excess of 268°C (9).

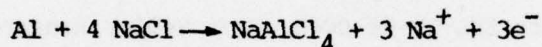
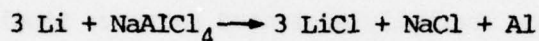
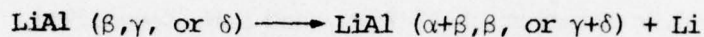
The study of the  $\text{CuCl}_2$  cathode (2) showed the optimum energy density was obtained using the 60.2 a/o LiAl alloy, a 50-100 mesh  $\text{CuCl}_2$  particle size, and 0.21 g graphite in the cathode. For a 48 a/o LiAl anode the best single cell delivered 27.9 W-Hr/lb to zero volts at a discharge rate of 15 mA/cm<sup>2</sup> at 225°C.

A detailed study was made on the effect of anode composition in these cells. The results indicate that the optimum anode was 60.2 a/o LiAl. Data for 48.0 a/o LiAl were noticeably inferior to those arising from the other powdered alloys tested. This reduced performance of the 48.0 a/o alloy was significant when analyzed in conjunction with:

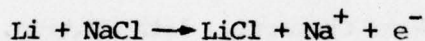
- a. the voltage spike phenomena observed during temperature activation for both the  $\text{CuCl}_2$  and  $\text{MoCl}_5$  cathodes,
- b. the observed 1.82 volt open circuit voltage compared to 1.80 volts for a pure Al anode,
- c. the reported behavior of LiAl alloy anodes in the LiCl-KCl eutectic electrolyte (10,11), and
- d. the phase diagram reported by Hansen (12), which has been further refined by Myles et al. (13). The data suggest that Li produced by dissociation of the various alloys reacts with the electrolyte to



produce Al, which is subsequently oxidized during discharge. The variations in the performances of the different powdered alloys were probably the result of differences in the stabilities of the various LiAl phases, with the  $\beta$  phase having a higher stability than either the  $\gamma$  or  $\delta$  phase alloys. A probable discharge mechanism for LiAl alloys in an NaCl-AlCl<sub>3</sub> electrolyte is:



and/or



Confirmation of this proposed mechanism will depend on analysis of single cell electrolytes after discharge and determination of the phase diagram for the LiCl-NaCl-AlCl<sub>3</sub> ternary electrolyte.

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## SOLID ELECTROLYTES WITH TETRAGONAL TUNGSTEN BRONZE STRUCTURE

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Solid electrolytes have high ionic conductivity ( $\sim 1 \text{ ohm}^{-1} \text{ cm}^{-1}$ ) and diffusion coefficient ( $\sim 10^{-4} \text{ cm}^2/\text{sec}$ ) at 'infinite' temperature and low activation energy ( $\sim 0.1 \text{ eV}$ ) for conductivity. They may be cationic or anionic depending on the mobile ion. Anionic conductors have appreciable conductivity only at high temperatures and activation energy nearing 1 eV. Their large activation energy may arise from their large size and also due to their participation in forming the framework within which the cations are placed. It is recognized that the structural aspects are the main factors which decide ionic conductivity of a compound. The anions are arranged to form a rigid lattice resulting in one, two or three dimensional paths for the mobile cation. The advantages of having higher orders of dimensionality for diffusion is discussed. Experimental techniques have been described. Ion exchange, N.M.R. line narrowing and vibrational spectroscopic methods may be used as screening techniques. Tracer diffusion, D.C. polarization, complex admittance and D.C. and A.C. conductivity measurements may be employed to characterize the solid electrolyte completely. Structural details and possibility of fast ionic conduction in tunnel structured compounds like hollandites, ramsdelite and tungsten bronzes particularly tetragonal tungsten bronze structure are discussed.



## NEW Na<sup>+</sup> AND Li<sup>+</sup> SUPERIONIC CONDUCTORS\*

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The discovery over a decade ago of fast Na<sup>+</sup>-ion transport in  $\beta$ -alumina has led to extensive efforts toward developing high-energy-density batteries, such as the Na/S battery, that use solid electrolytes (superionic conductors). Although the conductivity and stability of  $\beta$ -alumina meet the basic solid-electrolyte requirements of the Na/S battery, serious technological obstacles have been encountered in its utilization for practical ceramic membranes.

In view of these difficulties, several years ago our group at Lincoln Laboratory undertook a search for other fast Na<sup>+</sup>-ion conductors. We decided to look for oxides with three-dimensional transport, which might yield a higher ultimate conductivity than that of  $\beta$ -alumina, where transport is two-dimensional, with the Na<sup>+</sup> ions confined to widely separated layers. This search was guided by several important principles. Three-dimensional transport requires a crystal structure with a rigid "skeleton" network having an interstitial space that is interconnected in three dimensions, with the alkali ions located at sites within this interstitial space. For any appreciable conductivity these sites must be only partially occupied. For high conductivity, the activation energy for a jump from an occupied to an unoccupied site must be small. This requires the distance between adjacent sites to be relatively short and the "bottleneck" between sites to be large enough for easy passage of the mobile ion. Therefore the "radius" of the bottleneck should be at least as large as

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\* This work was sponsored by the National Science Foundation, Defense Advanced Research Projects Agency, and the Energy Research and Development Administration.

the sum of the radii of the mobile ion and the anion (in this case, oxygen) forming the rigid network. Furthermore, the bond between the mobile ion and the network anion should be as weak as possible; this can be accomplished by increasing the degree of interaction between the anion and the network cations.

By applying these principles we have discovered a material in the  $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$  system that has a  $\text{Na}^+$ -ion conductivity of  $0.4 \Omega^{-1} \text{cm}^{-1}$  at  $300^\circ\text{C}$ , as high as that of the best  $\beta$ -alumina at this temperature. This new material,  $\text{Na}_2\text{Zr}_2\text{PSi}_2\text{O}_{12}$ , has been named NASICON, for Na superionic conductor. If NASICON proves to be sufficiently stable for Na/S battery use, it will offer several significant advantages over  $\beta$ -alumina. Its sintering temperature ( $1230^\circ\text{C}$ ) is about  $300^\circ\text{C}$  lower, promising greater ease of fabrication. It is much less anisotropic and may therefore exhibit greater strength. In contrast to  $\beta$ -alumina, it is insensitive to water, so that handling and storage of membranes will be facilitated. Because of these possible advantages, NASICON is now under serious investigation by a number of laboratories in addition to our own.

Utilizing the same principles, we have recently undertaken a search for new  $\text{Li}^+$ -ion conductors. This search has already led to the discovery of the compound  $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ , which we have named LISICON, with a conductivity of  $0.13 \Omega^{-1} \text{cm}^{-1}$  at  $300^\circ\text{C}$ . This value exceeds by a factor of 4 the highest  $\text{Li}^+$ -ion conductivity previously reported for this temperature.

In conclusion, we believe that the development of NASICON and LISICON is significant not only in itself, but also because it demonstrates the existence of a number of principles that can be used to guide a systematic search for still better superionic conductors.

The views and conclusions contained in this document are those of the contractor and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the United States Government.

## NEW HEAVY-METAL SUPERIONIC CONDUCTORS

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High ionic conductivity at moderate temperatures is known for a large number of silver iodide complexes and for a smaller number of copper(I) halide complexes. We have studied the vibrational spectroscopy of some of these systems and have explored the possibility of ionic conductivity for other monovalent heavy-metal halides, namely those of  $\text{In}^+$  and  $\text{Tl}^+$ .

Our principal spectroscopic tool, Raman scattering, provides an indication of the onset of disorder, which is a characteristic of ionic conductors. As illustrated in the Figure for the known ionic conductor  $\text{Ag}_2\text{HgI}_4$ , disorder leads to a great broadening in the Raman spectrum, so Raman line broadening provides a convenient screening tool for potential heavy-metal halide ion conductors. We have applied this method in our search for  $\text{In}^+$  and  $\text{Tl}^+$  conductors. The pressure dependence of Raman frequencies, which affords a means of assessing the degree of anharmonicity for a vibrational mode, has been applied to  $\text{Ag}_2\text{HgI}_4$  and  $\text{Cu}_2\text{HgI}_4$ . The ca.  $85 \text{ cm}^{-1}$  Ag-I or Cu-I stretch was found to be strongly pressure dependent and was therefore concluded to be highly anharmonic. Temperature dependence for the Raman line widths of the  $85 \text{ cm}^{-1}$  band of the low-temperature (ordered) phases of  $\text{Cu}_2\text{HgI}_4$  and



$\text{Ag}_2\text{HgI}_4$  also indicates strong anharmonicity in the Cu-I stretch.

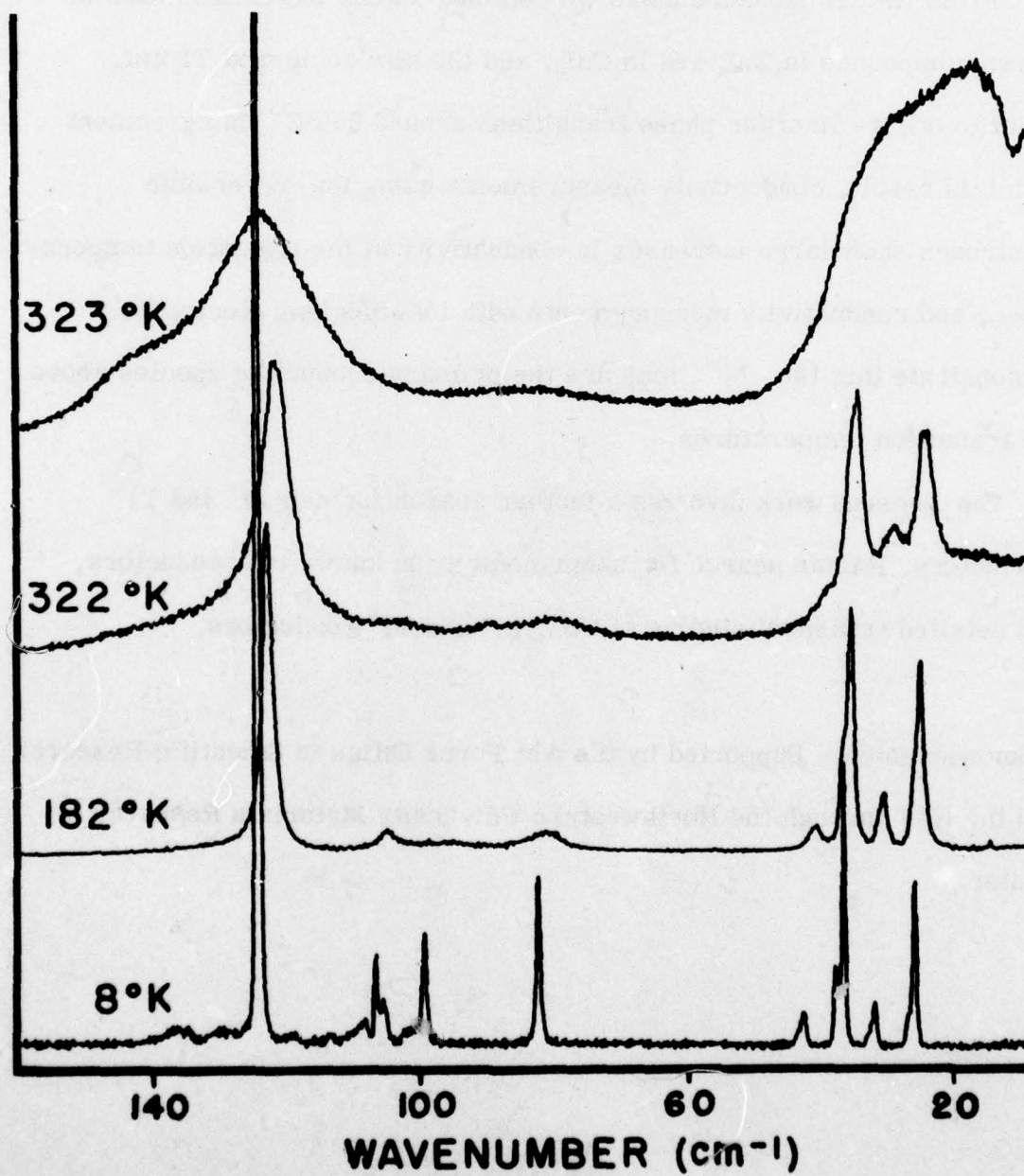
Anharmonicity of the type observed here may be an important contributor to the low activation energy for ion transport in the heavy-metal ion conductors.

From Raman measurements we obtained strong indications that the known compounds  $\text{In}_2\text{ZnI}_4$  and  $\text{In}_4\text{CdI}_6$ , and the new compound  $\text{Tl}_2\text{ZnI}_4$  undergo order-disorder phase transitions around  $250^\circ\text{C}$ . In agreement with this result, conductivity measurements using ion-reversible electrodes show large increases in conductivity at the transition temperatures, and conductivity measurements with ion-blocking electrodes demonstrate that the  $\text{M}^+$  ions are the primary conducting species above the transition temperatures.

Our present work involves a further search for new  $\text{In}^+$  and  $\text{Tl}^+$  conductors, Raman search for anharmonicity in known ion conductors, and detailed transport studies of  $\text{Cu}^+$ ,  $\text{In}^+$  and  $\text{Tl}^+$  conductors.

Acknowledgment: Supported by the Air Force Office of Scientific Research and the NSF through the Northwestern University Materials Research Center.

Raman spectrum of  $\text{Ag}_2\text{HgI}_4$  in the ionic conducting state ( $323^\circ\text{K}$ ) and low conductivity state ( $322^\circ\text{K}$  and below).



## ANALYSIS OF THE TRANSIENT BEHAVIOR OF POROUS ZINC ELECTRODES

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A mathematical model of porous zinc electrodes has been proposed. The model predicts the local charge transfer reaction rate  $j$ , current density in the solution phase  $i_2$ , potential in the solution  $\phi_2$  and in the matrix  $\phi_1$ , concentrations of potassium hydroxide  $c_A$  and potassium zincate  $c_B$ , volume fractions of zinc  $\epsilon_{Zn}$  and zinc oxide  $\epsilon_{ZnO}$ , and bulk solution velocity  $v^0$  as a function of time and position perpendicular to the electrode surface.

Experiments will be performed to measure the reaction profiles and the potentials of the discharged zinc electrodes. The effect of cycling on the reaction profiles and potential behavior will also be tested.

The theoretical and experimental results will be used to elucidate the causes of short time and long time failure of the zinc electrode. The clear understanding of failure of the zinc electrode will provide us with useful information to increase the cell capacity, as well as to guide future development in this area.



EFFECT OF COBALT HYDROXIDE COPRECIPITATION IN  
NICKEL HYDROXIDE ELECTRODES

by

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ABSTRACT

The performance of nickel hydroxide electrodes is greatly improved by the addition of cobalt nitrate to the nickel nitrate solution used in their formation by a cathodic deposition process. The object of this investigation was the elucidation of the mechanism of cobalt hydroxide in the electrode reaction.

A nickel microelectrode was designed to study charge-discharge under potentiostatic conditions. This electrode was used in the characterization of the cathodic deposition process for nickel hydroxide using cyclic voltammetry in water-ethanol mixtures. These studies indicate that the deposition of metallic nickel along with the deposition of nickel hydroxide could be a serious problem unless the electrode potential is made sufficiently negative to cause a considerable amount of hydroxide ion generation; this problem could occur at low current densities in a constant current deposition process. These studies also indicate that the nitrate ion is not a product of the nitrate decomposition process as hitherto believed.

Nickel hydroxide films were deposited onto the microelectrode surface by the cathodic deposition process in the presence and absence of cobalt nitrate; their behavior was studied by cyclic voltammetry, chronoamperometry, and chronocoulometry.

Cyclic voltammetric studies indicate that the mode of mass and charge transport through the nickel hydroxide film is diffusion controlled in the presence and absence of cobalt hydroxide; the diffusion coefficient, however, is several orders of magnitude less than that observed in fluid solutions. High noise levels observed in the cyclic voltammograms recorded when the charged material was present on the electrode surface indicate that the film impedance increases significantly in the charged state; this suggests that the battery active material behaves like a semiconductor in which the conductivity depends upon the state of charge. Most importantly, cyclic voltammetry reveals that cobalt hydroxide coprecipitation increases the reversibility of electron transfer in the charge-discharge cycle; in the absence of cobalt hydroxide a difference of 150 mV is observed between charge and discharge peak potentials; in the presence of ca. 10% cobalt hydroxide, this difference is only 75 mV. (See Figure 1)

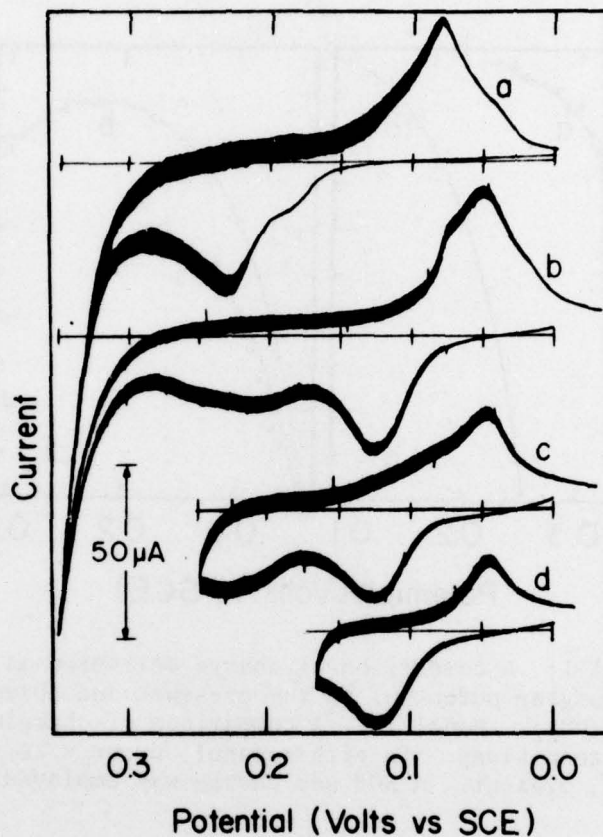


Figure 1. Slow scan cyclic voltammetry of 30% KOH solutions at the nickel hydroxide electrode. Curve a: containing no coprecipitated  $\text{Co(OH)}_2$ . Curves b, c, and d: containing  $\text{Co(OH)}_2$  coprecipitated from 1.8 M  $\text{Ni(NO}_3)_2$  containing 0.18 M  $\text{Co(NO}_3)_2$ . The scan rate employed was 0.5 millivolt/sec. The solutions were stirred during the recording of these scans.

Chronoamperometric studies at various fixed charging potentials reveal that the coprecipitation of cobalt hydroxide increases the rate of charge significantly. The magnitude of the charge accepted by the microelectrode is increased in the presence of cobalt hydroxide, also; this is probably due to thicker film formation when cobalt is present.

Chronocoulometric studies show that the microelectrode may be fully charged under potentiostatic conditions within 500 sec. (See Figure 2)

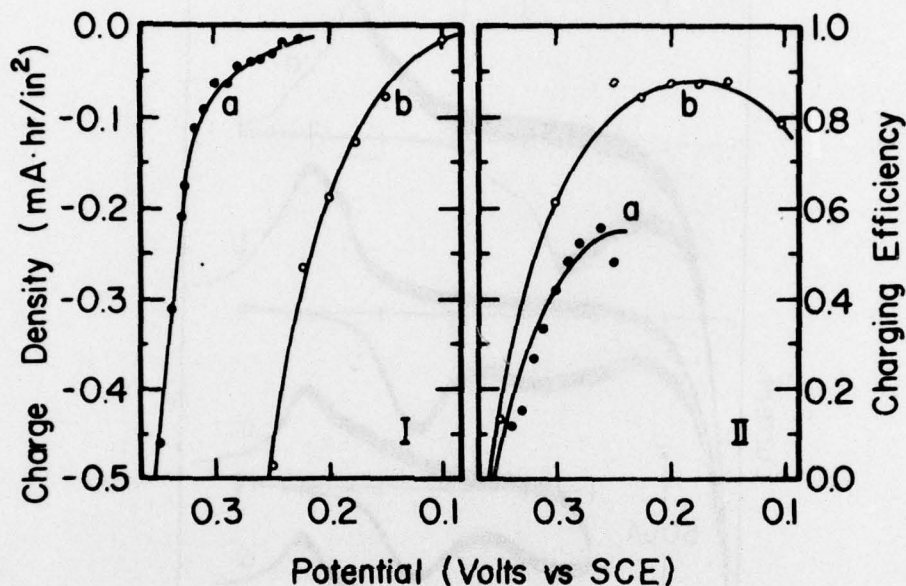


Figure 2. Panel I: A comparison of charge delivered as a function of electrode charging potential in the presence and absence of coprecipitated  $\text{Co(OH)}_2$ . Panel II: A comparison of charging efficiency under the same conditions. In either panel, curve a is for  $\text{Co(OH)}_2$  absent; curve b, present. A 500 sec charge was employed throughout.

The potential regime of efficient charge acceptance is 0.10 volt broader in the presence of cobalt hydroxide. The efficiency of charge recovery approaches 90% in this potential regime in the presence of cobalt hydroxide; in its absence, the maximum recovery observed was less than 60%, presumably due to the parasitic oxidation of solvent at the potentials sufficiently positive to induce charge in the absence of cobalt. From the magnitude of charge recovered, the thickness of the nickel hydroxide film is ca.  $2.5\mu$  in the presence of cobalt. In its absence, the film is believed to be no more than  $200\text{ m}\mu$  thick.



X-RAY PHOTOELECTRON AND AUGER SPECTROSCOPIC STUDY OF THE  
UNDERPOTENTIAL DEPOSITION OF Ag AND Cu ON Pt ELECTRODES

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The underpotential deposition of monolayer quantities of Ag and Cu has been studied using XPS and Auger spectroscopy. XPS chemical shifts of -0.65 and -0.95 eV vs. the bulk metal have been observed although no distinction was noted between the various underpotential states present in the cyclic voltammogram. The shifts were identical to vapor deposited submonolayer films of Ag and Cu on Pt in the low coverage ( $\theta \sim 0.1$ ) limit. A gradual shift with coverage for the underpotential deposit indicated that islanding was present only in the evaporated films. Measurement of the Cu and Ag Auger spectra gave results independent of the surface work function when compared to the XPS spectra. Interpretation of this Auger parameter is, however, at present ambiguous.

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## ELECTROCHEMICAL STUDIES AT THE STATE UNIVERSITY OF NEW YORK AT BUFFALO

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Air Force sponsored electrochemical research at the State University of New York at Buffalo in the past two years has involved four major areas. These are summarized below.

- I. Underpotential Metal Deposition - (UPD)
  - A. Isotherm Determination of Ag on Au and Ag on Au
    1. Net charge in UPD species
    2. Number of atom layers at  $E_{\text{Nernst}}$ .
  - B. Open-circuit UPD Formation of Ag on Au, and Hg on Au.
    1. Coulostatic mechanism
    2. Heterogeneous chemical mechanism.
- II. Model Corrosion Studies
  - A. Single Phase System
    1. Ni-Cu
  - B. Multiphase System
    1. Hg-Sn-Ag Amalgam
- III. Current Distribution in Multielectrode Systems
  - A. Ring-Electrode
  - B. Ring-Disk Electrode (RDE)
- IV. Electrode Kinetics
  - A. CO on platinum
  - B. O<sub>2</sub> reduction
    1. Effect of UPD deposition
    2. Effect of "poisons"
  - C. Sinusoidal hydrodynamic modulation at the rotating disk electrode (SHMRDE).

The presentation was centered on recent theoretical and experimental SHMRDE studies.

Programming the rotation speed of the rotating disk electrode provides the electrochemist with a new variable to study electrode kinetics. One of the most useful programming functions is the one used in SHMRDE studies

$$\omega^{1/2} = \omega_0^{1/2} [1 + \epsilon \cos (p \omega_0 t)] \quad (1)$$

where  $\epsilon$  is a constant, usually chosen to be in the range  $0 \leq \epsilon \leq 0.2$ ,  $p$  is another constant usually chosen to be in the range  $0 \leq p \leq 1$ , and  $\omega_0$  represents the center rotation speed (i.e., the rotation speed when there is no modulation,  $\epsilon = 0$ ). Thus, a typical experiment might use the programming function

$$\omega^{1/2} = \omega_0^{1/2} [1 + 0.1 \cos (0.5 \omega_0 t)] \quad (2)$$

for center rotation speeds of 900, 1600, 2500, 3600, 4900 and/or 6400 RPM.

The corresponding current response will have a component of the form

$$i = i_{\omega_0} [1 + A \cos (p\omega_0 t - \phi)] \quad (5)$$

at the hydrodynamic modulation frequency  $p\omega_0$ , where  $i_{\omega_0}$  is the current observed at  $\omega_0$  in the absence of modulation and  $A$  and  $\phi$  are functions of  $p$ ,  $\epsilon$ , the Schmidt number and the mechanism and kinetics of the electrode process.

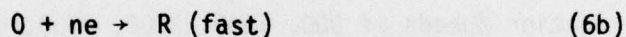
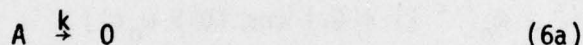
$\phi$  and  $A$  are conveniently measured by synchronous phase sensitive detection techniques, and can be determined even in the presence of non-convective diffusion controlled currents thousands of times greater than  $i_{\omega_0}$ . Analytical sensitivities in the  $10^{-7}$  N range are readily obtained,



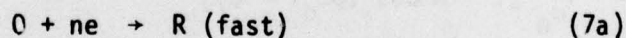
and good modulated current-potential curves are obtained in  $10^6$  N solutions under conditions where the conventional current-potential curve is completely distorted by surface redox processes.

The theoretical treatment of kinetic phenomenon at SHMRDE required solving the appropriate convective diffusion problem while taking into account the time varying rotation speed specified by eq. (1). In general, closed form solutions for the various problems are not possible and numerical methods have been developed which yield  $A$  and  $\phi$  values in a form suitable for obtaining quantitative kinetic information.

A variety of problems have been treated theoretically. Among these are the case of (a) pure convective-diffusion (2); (b) finite electron transfer rate (3); (c) the reaction sequence



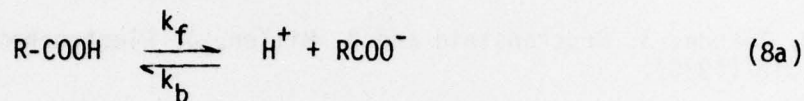
corresponding to the conversion of a non-electroactive species by a first order process into an electroactive species which then undergoes fast electron transfer (4); and (d) the catalytic sequence (4)



This theory was discussed and its experimental verification given for (a) slow electron transfer case using the Fe(III)/Fe(II), Tl(III)/Tl(I), and  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  systems (5), and (b) the prior chemical reaction case, eqs (6a-6b) for the dissociation of weak acids (6).

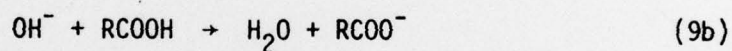
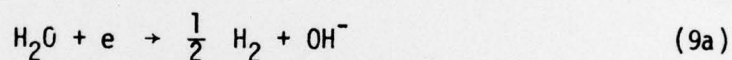
At the early part of limiting current region, the SHMRDE results

for the evolution of hydrogen from formic acid/formate buffers agree with the classical model of Vielstich and coworkers (7):



where  $k_f$  has a value to make (8a) rate controlling.

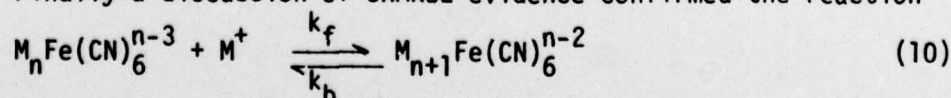
The SHMRDE results for the dissociation rates of formic, acetic and propionic acids in the cathodic portion of the limiting current region disagree with the results obtained with the RDE method. This difference was shown to arise from the reactions



which are readily detected by the SHMRDE method, and easily overlooked using the conventional RDE techniques.

In the potential region where reactions (9a) and (9b) are not occurring the value of  $k_b$  calculated for acetic acid and propionic acid were several order of magnitudes larger than the limiting diffusive controlled rate for a second order process. Our theory is based on the reaction layer concept, and these experimental results indicate that the CE theory probably does not apply for these two acids.

Finally a discussion of SHMRDE evidence confirmed the reaction



first suggested by Peter, et.al. (8).

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## NUMERICAL DIFFERENTIATION OF SURFACE TENSION DATA

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A short introduction described the electrochemical research program at Georgetown University, probing into the double layer structure, and the major experimental tools used: Fourier-transform cell impedance measurements<sup>1,2</sup>, surface tension determination by the maximum bubble pressure method<sup>3,4</sup>, and kinetic probe measurements using the reduction of perbromate anions<sup>5</sup>. The relative advantages and limitations of these various techniques were mentioned; the cell impedance measurement appears to be the most generally applicable one, with obvious applications in, e.g., the determination of the state of charge of batteries of interest to the Air Force<sup>6</sup>.

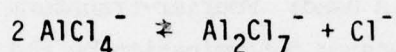
Subsequently, the novel use of Fourier transformation in the numerical differentiation and smoothing of surface tension data was described in detail. The main advantage of this method is that the optimum trade-off between noise reduction and signal distortion can be determined with a rather objective criterion, based on the power spectrum of the original data set. Examples of single and double differentiation were given, based on both synthetic and actual, experimental data, and compared with the results of the alternative procedure using a least-squares fit to a moving polynomial<sup>7</sup>.

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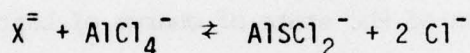
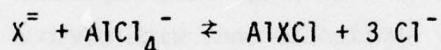
## ELECTROCHEMISTRY IN MOLTEN CHLOROALUMINATES

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We have been concerned recently with acid-base dependent chemistry and electrochemistry in molten  $\text{NaAlCl}_4$ . In particular, the primary acid-base reaction in these melts may be written as -

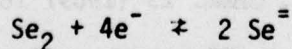


We have recently found that  $\text{O}^{2-}$  and the chalcogenides, S, Se, Te react with the solvent in accordance with the following equilibria:

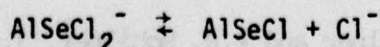


That is, the oxide and chalcogenide dianions behave as di- or tribases, depending on the melt acidity. Potentiometric and titrimetric procedures have been employed to evaluate the basic strength of the dianions, which is in the order  $\text{O}^{2-} > \text{S}^{2-} > \text{Se}^{2-} > \text{Te}^{2-}$ . Essentially, the bases function as tribases as the melt is made progressively acidic. These observations explain why certain metal sulfides, for instance, are insoluble in the basic melt but soluble in acid. Metal oxides, on the other hand, do not form readily in the melt because the  $\text{AlOCl}$  (or  $\text{AlOCl}_2^-$ ) formation results in the conversion - at least from the thermodynamic point of view - of the oxide into chloride.

The electrochemistry of selenium has been studied in some detail in the melt. From potentiometric and coulometric studies it appears that the reaction



is potential determining. The change in potential of the  $\text{Se}_2/\text{Se}^{2-}$  couple with melt acidity permits the determination of the equilibrium



Se can be oxidized to a +2 and +4 species, depending on the melt acidity.

The kinetics of the electrode processes have been studied.

The electrochemistry of Mo(V) has been studied in some detail since this material has promise as a thermal battery cathode. The reduction to the +3 state appears to involve the formation of Mo(IV) which can then disproportionate. From potentiometric measurements, it appears as if two chlorides are liberated during the Mo(V) to Mo(III) reduction. Reduction below the Mo(III) state is very complex and appears to involve considerable surface chemistry; Mo(II) may well be formed, but its solubility is very low and experiments with rotating ring-disc electrodes have indicated only that complex surface chemistry exists.

$\text{NiCl}_2$  is insoluble in the basic melts, and the system  $\text{Ni/NiCl}_2/\text{Cl}^-$  functions as a second-class electrode and can be used for measurement of melt pCl over a limited range. Contrary to published reports, the precipitate formed when an acid melt, containing both oxide and Ni(II), is made basic is  $\text{NiCl}_2$  and not NiO.

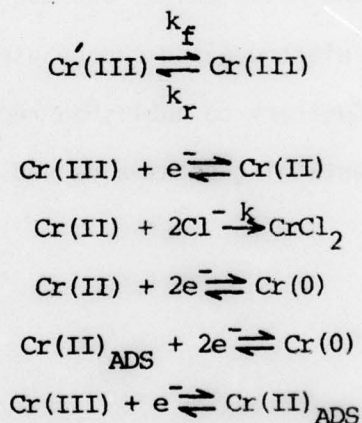


FJSRL RESEARCH PROGRAM IN ALUMINUM CHLORIDE FUSED SALT CHEMISTRY

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The research program in fundamental electrochemistry underway in our laboratory is designed to support both our aluminum chloride primary thermal battery research and an effort aimed at devising new types of low temperature secondary cells based on aluminum chloride containing electrolytes. This program has been tailored specifically to address typical problem areas in the selection and utilization of components for both types of cells. Areas of investigation include: electrode kinetic studies of the reduction mechanism of potential cathode materials, concentration cell modeling of processes occurring at aluminum anodes, and electrolyte studies.

Electrode kinetic studies of the reduction of  $\text{CrCl}_3$  in NaCl-saturated  $\text{AlCl}_3$  have recently been completed. Stationary and rotating electrode voltammetry, chronamperometry, and coulometry were used to deduce the Cr(III) reduction mechanism at a glassy carbon electrode at 175°C:



Low valent states of chromium and related transition metal halides are under consideration as cathodes for FJSRL battery systems. Studies of this type provide detailed information on the discharge mechanism that would be expected in a practical battery system.

Electromigrational depletion chronopotentiometric studies of aluminum anodization in fused NaCl- $\text{AlCl}_3$  have been undertaken in an effort to better understand the processes which occur at the anode in thermal batteries. Various concentration cell equations have been examined in an attempt to model EMF changes with time during discharge. The concentration cell models examined are those based on the integral expression for the EMF of a concentration cell with transference (1-3) and those based on the Nernst equation (2). Particular emphasis has been placed on calculating excess EMF contributions from vapor pressure data for the former expression.

In addition to the vapor pressure data just cited for NaCl-AlCl<sub>3</sub> mixtures, the vapor pressures of pure AlCl<sub>3</sub> liquid and solid have been measured (4), and the P, V, T behavior of gaseous AlCl<sub>3</sub> investigated. Other work is underway on electrolytes, including measurement of ionic conductivity of NaCl-AlCl<sub>3</sub> melts and the density and ionic conductivity of LiCl-AlCl<sub>3</sub> mixtures. Binary and ternary phase diagrams of several alkali chloride - aluminum chloride mixtures are also being determined.

Electrolyte studies concerning a new class of room temperature molten salt mixtures, 1-alkylpyridinium chloride-aluminum chloride have recently been undertaken. Determination of the density, viscosity, and conductivity as a function of temperature have been completed for the 1-methyl-, 1-ethyl-, 1-propyl-, and 1-butylpyridinium chloride pure molten salts as well as the corresponding 2:1 molar ratio aluminum chloride: 1-alkylpyridinium chloride molten mixtures.

In addition to in-house research previously described, FJSRL supports Professor Harold Øye, Norwegian Institute of Technology, Trondheim, Norway. Professor Øye has been measuring the viscosity as a function of composition for various alkali chloride-aluminum chloride fused salt mixtures.

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