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BASIC AND APPLIED RESEARCH IN  
MATERIALS

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## I. SUMMARY

This report covers the period from 1 June 1973 through 30 November 1973 and describes the research initiated in four major areas: 1) Materials for Energy Storage, 2) Heterogeneous Catalysis, 3) Maximization of Electret Effect in Polyacrylonitrile Films and 4) Properties of Foils Containing Very Short Wavelength Composition Modulations.

### A. Technical Problem and Approach

#### 1. Materials for Energy Storage

The discovery of new types of solid electrolytes (such as beta alumina,  $\text{RbAg}_4\text{I}_5$ , copper and silver halides and stabilized zirconia) with large values of ionic conductivity at relatively low temperatures has enhanced the prospect of developing battery systems possessing a high energy storage-to-weight ratio, high power output capability, long life in service, efficiency in charge-discharge characteristics and the capability of being constructed from inexpensive, readily obtainable materials. Two complementary areas of research are being pursued. The first involves a search for new materials to be used as solid state electrolytes and electrodes, and the second involves detailed studies on electrolytes already known to be predominantly ionic conductors. Toward these ends, studies already underway of cuprous halides as model systems are being continued. Research has been initiated on materials (e.g.,  $\beta$  and  $\beta''$  alumina, some tungsten bronze phases, calcia stabilized zirconia, and some hollandites) which can be used over a wider range of operating conditions. Materials of interest will be prepared by sintering as well as by standard crystal growth techniques. Mossbauer and NMR techniques as well as electrical conductivity and dielectric loss properties are being used to characterize these materials.

#### 2. Heterogeneous Catalysis

A number of the most important heterogeneous catalysts consist of tiny crystallites of metal supported on carriers such as alumina or silica. Yet relatively little is known of the effect of particle size and morphology and of the effect of the support upon the catalytic activity. Standard batches

of catalysts are being prepared by different methods, of varying particle sizes and on different supports. These catalysts will be characterized as completely as possible using x-ray photoelectron spectroscopy (to gain information about the surfaces, i.e., support, catalyst, etc.), EPR studies (to yield information about the identity of sites at the surface and their electronic nature), kinetic studies (to determine the kinetic form and rate constants for reactions chosen to give optimum information about catalytic characteristics) and selectivity studies (to determine relative yields of several concurrent reactions). When these data have been assembled, an attempt will be made to systematize the results phenomenologically and to develop a theoretical understanding of the underlying phenomenon.

### 3. Maximization of Electret Effect in Polyacrylonitrile Films

Dielectric solids possessing a permanent electric field (electrets) can potentially be used as active elements in a number of devices, e.g., acoustical transducers, infrared detectors, piezoelectric devices and optical second harmonic generators. Polymeric solids make superior electrets because of their thermal and mechanical stability, long chain macromolecular nature (which afford an additional means of orienting dipolar groups) and low cost. These properties will be exploited in the creation of new materials for use in apparatus utilizing the electret effect.

The purpose of the present research is to maximize the electret-related behavior of polyacrylonitrile film using selective modification of physical and chemical microstructures and to gain an understanding of the effect of morphology on the electret effect in polymer solids in general. Initial research is directed toward determining relationships between physical modifications and the magnitude of their effect on the electret effect in polyacrylonitrile. Samples will be prepared both by solution casting and by heating to temperatures above the glassy transition and then cooling in the presence of an electric field. The magnitude of the electret effect produced will be measured and the molecular organization characterized.

### 4. Properties of Foils Containing Very Short Wavelength Composition Modulations

Copper-nickel foils containing very short wavelength (7-60 Å) composition modulations exhibit a surprising increase in ultimate strength and

elastic modulus as the wavelength of the modulation is decreased. There appear to be no theories that account for this increase. The present research is directed toward investigating systems other than Cu-Ni to determine whether the effect is limited to this material and, if not, to develop systems which exhibit even higher elastic moduli. Attempts will be made to extend the range of wavelengths downward from the present 14 Å to 7 Å (which is the smallest wavelength composition attainable with the present setup). A further objective is the fabrication of small components of intricate shape having high strength to weight ratios. Preliminary electrical and magnetic measurements will also be undertaken.

## B. Technical Results

### 1. Materials for Energy Storage

The partial conductivities of Ca-stabilized  $ZrO_2$  solid electrolytes have been measured over a wide range of  $p_{O_2}$  in the temperature range of 900°C to 1200°C and definitive limits of  $p_{O_2}$  established for the satisfactory operation of this electrolyte at temperatures up to 1200°C. Sodium activities in sodium tungsten bronze have been measured and the partial molar thermodynamic qualities of Na in the tungsten bronze determined.

Hollandite type solid electrolytes have been produced by the electrolysis of molten oxides which exhibit good ionic conductivity along the c-axis and poor conductivity perpendicular to this axis. Hydrostatically pressed and sintered rods of hollandite-type phases are being prepared preparatory to growing single crystals of these phases. Work has begun on developing NMR techniques for studying ion motion. The cation radial density function is being studied to gain insight into the mechanism governing the high cationic mobility in CuCl. Three samples of  $\gamma$ -CuCl have been prepared with different isotopic composition of the Cu component. Preliminary data using neutron diffraction patterns have been obtained using the reactor at the Argonne National Laboratory. These studies are being continued in order to gather data to test various models for CuCl.

The electronic properties of CuI are under investigation using dc polarization and ac conductivity measurements to gain information on the ionic



conductivity. The redistribution time of electron holes in CuI is also being studied.

## 2. Heterogeneous Catalysis

The necessary amounts of silica gel have been prepared by sieving and have been washed in  $\text{HNO}_3$  and dried. Furnaces and furnace tubes for catalyst reduction have been assembled and tested, and one 100 gm batch of impregnated catalysts has been prepared.

An apparatus for the measurement of dispersion by chemisorption has been assembled and is being tested. A small-angle rig for x-ray studies of the catalysts has been constructed and tested, and preliminary surface area measurements on activated charcoal have almost been completed. In addition, an apparatus to study the kinetics of exchange of cyclopentane with deuterium has been constructed.

## 3. Maximization of Electret Effect in Polyacrylonitrile Films

A special test cell in which samples can be polarized and the magnitude of the polarization measured has been constructed and refined for stability in current, voltage and temperature. Polarized specimens of polyacrylonitrile have been prepared in this cell, both stretched and unstretched. Preliminary results indicate that stretching during poling increases the magnitude of the electric polarization. Furthermore, over certain frequencies, films thus prepared vibrate at twice the frequency of an impressed electric field.

## 4. Properties of Foils Containing Very Short Wavelength Composition Modulations

A new bulge testing apparatus for determining stress-strain curves has been designed and is under construction. A numerical calculation has been made and an exact solution obtained which will permit proper analysis of the strain in bulge-tested specimens. Work has also commenced on preparing copper-palladium foils.

## II. RESEARCH REPORTS

A. Materials for Energy Storage

## Faculty:

- D. H. Whitmore, Professor, Materials Science, Group Leader
- D. L. Johnson, Professor, Materials Science
- L. H. Schwartz, Professor, Materials Science
- J. B. Wagner, Professor, Materials Science
- L. B. Welsh, Assistant Professor, Physics

## Research Staff:

- H. M. Lee, Visiting Scientist, Materials Science

## Graduate Students:

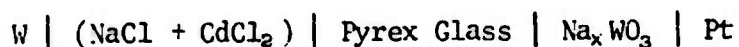
- D. Bouchon, Materials Science
- D. Girard, Materials Science
- T. Jow, Materials Science
- J. Schreurs, Materials Science

1. Transport Number Measurements of Ca-Stabilized  $ZrO_2$  Solid Electrolytes at Elevated Temperatures

The partial conductivities of Ca-stabilized  $ZrO_2$  solid electrolytes have been measured over a wide range of  $p_{O_2}$  within the temperature region 900° to 1200°C. Following a suggestion by Heyne, the sides of the polarization cell were closed off with Pt to prevent the leakage of oxygen ions by exchange with the surrounding gas atmosphere. The magnitudes of the partial conductivity values, as well as their dependence on  $p_{O_2}^{\frac{1}{4}}$  at fixed temperature, agreed well with the earlier findings of Patterson et al. [J. Electrochem. Soc. 114, 752 (1967)]. The present study increased the temperature range of these earlier observations by 200° and permitted definitive limits of  $p_{O_2}$  to be established for the satisfactory operation of Ca-stabilized  $ZrO_2$  as a solid electrolyte at temperatures up to 1200°C.

## 2. Thermodynamic Study of Cubic Sodium Tungsten Bronze by the EMF Method

Sodium activities in  $\text{Na}_x\text{WO}_3$  have been measured with the help of the galvanic cell:



in which pyrex glass acted as a solid electrolyte for  $\text{Na}^+$  ions, and a molten mixture of  $\text{NaCl}$  (40%) and  $\text{CdCl}_2$  was employed as the reference electrode. To prevent the loss of sodium, the  $\text{Na}_x\text{WO}_3$  electrode specimens were contained in a closed compartment. Measured e.m.f. values exhibited closely linear relationships with temperature from  $400^\circ$  to  $600^\circ\text{C}$ , from which partial molar thermodynamic qualities of Na in the tungsten bronze phase could be determined.

## 3. Single Crystal Synthesis of Hollandite Type Solid Electrolytes

The electrolysis of molten oxides is being used to produce a number of small single crystals of compound phases of general composition  $\text{A}_x\text{BO}_2$ , where A is an alkali-metal ion, and B represents a mixture of  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$  or of  $\text{V}^{3+}$  and  $\text{Ti}^{4+}$ . Among these phases are the hollandite types  $\text{K}_x\text{Ti}_4\text{O}_8$  and  $\text{Cs}_x\text{Ti}_4\text{O}_8$ . On the basis of preliminary observations, the latter phase appears to have interesting electrical characteristics, exhibiting good ionic conductivity along the c-axis and poor conductivity perpendicular to this axis, suggesting that  $\text{Cs}^+$  ions may be diffusing rapidly down channels parallel to the c-axis. Moreover, the activation energy for this ionic transport is approximately the same ( $\approx 5$  kcal/mole) as has been found for other fast ion conductors like beta alumina. Ion exchange experiments will be undertaken soon for the purpose of substituting other alkali ions for either the  $\text{Cs}^+$  or  $\text{K}^+$  ions in the above hollandite phases prepared electrolytically. In addition hydrostatically-pressed and sintered rods of several hollandite-type phases are being prepared for use with a hollow-cathode, floating-zone method to attempt the preparation of single crystals of these phases.

## 4. Nuclear Magnetic Resonance Diffusion Studies in Solid Electrolytes

Work is beginning on the development of suitable NMR techniques for studying ion motion (using  $\text{Na}^{23}$ ,  $\text{Li}^7$ ,  $\text{Cu}^{63}$  etc.) in oxide solid electrolytes exhibiting channel structures. Motional line-narrowing studies with a wide-line spectrometer operating at a fixed frequency and measurement of the



spin-lattice relaxation time  $T_1$  in the vicinity of the  $T_1$  minimum using pulse-type measurements are being emphasized.

#### 5. Determination of the Cation Radial Pair Density Function in $\gamma$ -CuCl at Elevated Temperatures

The cation radial pair density function is being studied to gain insight into the mechanism governing the high cationic mobility in CuCl, taken here as a prototype for halide ionic conductors. Three samples of  $\gamma$ -CuCl (F43m) have been prepared with different isotopic composition of the Cu-component: 99.7% Cu-63, natural Cu, and 99.7% Cu-65. Powder neutron diffraction patterns were taken at 25°C and at 366°C up to  $\sin \theta/\lambda = .8 \text{ \AA}^{-1}$ . The Fourier Transform of the coherent differential scattering cross section curves is a known function of the radial pair density functions for CuCu, CuCl, and ClCl. From the positions of the atoms in the unit cell, two temperature factors and a series of coupling factors, one can, with a gaussian broadening, calculate the radial density functions generated by the model (Kaplow et al. 1964). The model at the basis of the fit remains the sphalerite structure. A least squares fitting procedure, with calculated termination error, reveals a striking difference between the CuCu and the ClCl partial densities: the ClCl curves show well resolved density peaks out to large distances, while the CuCu-curves exhibit only one main maximum, followed by rapidly damped oscillations about the average density. A comparison between integrated intensity analysis (II) and radial density analysis (RD) shows that the incorporation of the diffuse scattering in the latter affects primarily the temperature factor of the Cu-atom. With  $d =$  first neighbor distance,  $\delta = \langle u^2 \rangle^{1/2}/d$  at 25°C is found to be 0.17 for Cu and 0.11 for Cl (II) or 0.26 for Cu and 0.11 for Cl (RD). The values at 366°C are found to be 0.29 and 0.15 (II) or 0.41 and 0.18 (RD).

#### 6. Electronic Conductivity and Mobility of Electronic Charge Carriers in Cuprous Iodide

In an extension of studies on CuBr and CuCl the electronic properties of CuI are being investigated using a d.c. polarization technique on a cell of the form Cu | CuI | graphite and a.c. conductivity on a cell of the form Cu | CuI | Cu. The a.c. conductivity yields the total conductivity,  $\sigma_{\text{total}} = \sigma_{\text{ionic}} + \sigma_{\text{electronic}}$ . Results on pressed compacts agree well with

the earlier data of J. Wagner and C. Wagner. However, the Arrhenius plot is non-linear, suggesting that more than one type of defect may be contributing to the ionic conduction. The d.c. polarization measurements yield the electronic conductivity. The data show the ratio of  $\sigma_{\text{electronic}}/\sigma_{\text{ionic}} \cong 10^{-3}$  at 300°C to 350°C. The redistribution time for electron holes when a sample is biased suddenly from one voltage to another is being studied.

#### B. Heterogeneous Catalysis

##### Faculty:

- R. L. Burwell, Professor, Chemistry, Group Leader
- J. B. Butt, Professor, Chemical Engineering
- J. B. Cohen, Professor, Materials Science
- B. M. Hoffman, Associate Professor, Chemistry
- J. E. Lester, Assistant Professor, Chemistry

##### Research Staff:

- T. Uchijima, Postdoctoral Research Associate, Chemistry

##### Graduate Student:

- C. Sorrentino, Chemical Engineering

A number of the most important heterogeneous catalysts consist of tiny particles of metal supported upon a carrier such as silica or alumina. Yet, relatively little is known of the effect of particle size and morphology and of the effect of the support upon the catalytic activity, either descriptively or theoretically. In the present project, the approach has been to prepare batches of standard catalysts by different methods, of varying particle sizes and supports; they are being characterized as completely as possible by physical methods and then evaluated by studying the effects of several heterogeneous catalytic reactions upon these catalysts. When these data have been assembled, an attempt will be made to systematize the results phenomenologically and thenceforth to develop a theoretical understanding of the underlying phenomena.

The catalytic reactions studied will include some which are not too sensitive to the details of catalyst dispersion (percent of atoms of metal which are on the surface) as well as some which exhibit the maximum possible variation with dispersion, support, etc. At the present time it is not possible to select those reactions a priori, and some changes in the present choice of reactions may be needed as information becomes available.

Platinum catalysts were chosen as a starting point because there is more background information available for them than for most other catalysts. Initial studies will be made on platinum supported on silica, with platinum supported on alumina to be studied later. Each type will be prepared by two different methods, in both sintered and unsintered forms. Davison Grade 62 silica gel was chosen as the silica support, and W. R. Grace and Co. has provided 200 pounds of this gel in the form of 60-200 mesh particles. Catapal alumina (a very high purity alumina) has been chosen as the alumina support; the Continental Oil Company has agreed to supply this material. Catalysts will be prepared by ion exchange with  $\text{Pt}(\text{NH}_3)_4^{2+}$  and by impregnation with chloroplatinic acid with, in both cases, ensuing reduction.

During the period since the initiation of this project, the necessary amounts of sieved silica gel have been prepared by sieving on standard laboratory sieves. The resulting gel was first washed with 0.01 M  $\text{HNO}_3$ , then with water and finally dried. The washing removes sodium ions from the gel as well as fines which cling to larger particles. This was a very tedious job and required several man months of effort. In addition, preliminary experimental development work on catalyst preparation has been undertaken. Furnaces and furnace tubes for catalyst reduction have been assembled and tested, and one 100 g. batch of impregnated catalyst has been prepared.

For the physical characterization of the catalysts an apparatus for the measurement of dispersion by chemisorption has been assembled and is being tested. In this apparatus, one measures the amount of hydrogen chemisorbed on the catalyst after purging in helium at 400°C. (It is assumed that each surface platinum atom adsorbs one atom of hydrogen.)

During the forthcoming year the catalysts will be examined by means of x-ray techniques. Thus far, a small-angle rig especially designed for

this task has been constructed and tested, and preliminary surface area measurements on activated charcoal have almost been completed. A special sample cell which can either be evacuated or filled with gas has also been constructed.

An apparatus to study the kinetics of exchange of cyclopentane with deuterium has been completed. The purpose of these studies is to test the relation between the structure of the platinum catalysts and the yield using a reaction analogous to the hydrogenation of olefins.

C. Maximization of Electret Effect in Polyacrylonitrile Films

Faculty:

S. H. Carr, Associate Professor, Materials Science

Graduate Student:

R. Comstock, Materials Science

Piezoelectric and pyroelectric properties of electrically polarized polymers are currently being exploited by using them as active elements in vibration transducers and heat detectors. The fundamental origin of this effect is due to dipolar moieties along each chain having a net orientation in a given direction. At the present time, however, selection of which polymers to place in which application is determined largely by searching for a material with optimum performance. Because little is known about relationships between molecular organization and net electrical polarization, no appreciable efforts have been expended in trying to control polarization properties in a single polymer solid through physical means. Thus, the research involved here has sought to characterize such relationships in films made from a highly polar polymer, polyacrylonitrile.

At the present time, electrically polarized specimens of polyacrylonitrile are being made in a special test cell that also has capability of measuring the magnitude of permanent polarization produced during poling. This cell has been refined to the point that it is stable in both current and voltage to one part in  $10^5$  and temperature to one part in  $10^3$ . The

temperature can be varied from 80°K to 480°K at rates up to 10°K/min. Most significantly, specimens are mounted in movable grips and therefore can be stretched whenever desired. Preliminary analysis of polarized polyacrylonitrile has revealed that stretching during poling results in increased magnitude of electric polarization. It has further been found that over a particular range of frequencies, films of polyacrylonitrile prepared as described above will vibrate at double the frequency of an impressed electric field.

#### D. Mechanical Properties of Composition Modulated Foils

Faculty: J. E. Hilliard, Professor, Materials Science

Graduate Student:

T. Tsakalakos, Materials Science

Several years ago Professor Hilliard developed a technique for producing thin foils ( $\sim 0.5 \mu\text{m}$ ) containing one-dimensional short wavelength ( $8 - 80 \text{ \AA}$ ) composition modulations. The foils were initially used for an investigation of diffusion over very short distances. However, it later became apparent that they were well suited for studying the effect of structure on properties in general because the structure (in terms of the amplitude and the wavelength of the modulation) was well defined and easily controlled.

Professor Hilliard and one of his students have already made rather extensive studies of the mechanical and electrical properties of copper-nickel foils. Under the current program, these studies are to be extended to copper-palladium modulated foils with the objective of testing Cahn's theory of strengthening produced by spinodal decomposition. Cahn [Acta Met. 11, 1275 (1963)] proposed a theory which accounted for the increase in strength of an alloy undergoing spinodal decomposition. Such an alloy has composition fluctuations which can be described by stationary plane waves. These composition fluctuations possess both amplitude and wavelength. When the foils containing such spinodal composition fluctuations are annealed (aged), the wavelengths are affected by the temperature while the amplitude is affected by the annealing time. There is an analogy between the resistance of the



passage of a dislocation through a material containing precipitates and the resistance encountered when the dislocation encounters composition gradients and internal stresses caused by spinodal decomposition. Copper and palladium have a large difference in atomic sizes; according to the theory, a composition modulation in this system should produce a very substantial increase in yield strength. Thus far, a new bulge testing apparatus has been designed and is currently under construction. While awaiting completion of the bulge tester, Mr. Tsakalakos has conducted a theoretical study to resolve certain conflicts in the literature on the analysis of the strain in bulge-tested specimens. By means of a numerical calculation he was able to obtain an exact solution to this problem. He has also concluded a study of the correction required to allow for the effect of the strong  $\langle 111 \rangle$  epitaxy present in the evaporated films.