**BASIC RESEARCH ON CERAMIC MATERIALS FOR ENERGY
STORAGE AND CONVERSION SYSTEMS**

Progress Report

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PROGRESS REPORT

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BASIC RESEARCH ON CERAMIC MATERIALS FOR ENERGY STORAGE AND CONVERSION SYSTEMS

Abstract

The present research program involves utilizing appropriate probes for movement of ionic and electronic charge carriers in ceramic materials suitable for solid electrolyte and electrode applications in high-performance, secondary battery and fuel cell systems. Special emphasis is placed on developing: (1) a better understanding of the effects of structure, impurities and composition on transport mechanisms; and (2) detailed knowledge of the kinetics and mechanisms of reactions occurring (on a microscopic scale) at the electrode-electrolyte interfaces of energy storage and conversion systems.

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During the first eight months of this program, considerable progress has been made in the areas of synthesis of materials, preparation of polycrystalline samples and the development of techniques for characterization of candidates for solid electrolyte applications in particular.

Initially, emphasis has been put on solid electrolyte candidates belonging to the oxide tunnel structure type (Li titanates exhibiting a ramsdellite structure and β alumina), some double halides ($\text{Li}_{1-2x}\square_x\text{Mg}_x\text{O}_1$), where $\square$ signifies a cation vacancy, and on complex salts and Prussian blue analogs containing the monopositive ions of group III, viz, Ga(I), In(I) and Tl(I). These latter salts are expected to be analogs of the best superionic compound known to date, RbAg_4I_5 . Examples of this last category of compounds would be In_2ZnI_4 and In_4CdI_6 in which it is expected the In^+ ion motion would be very rapid. To date, characterization studies have mainly involved Raman scattering experiments in the case of complex salts involving Ga(I), In(I) or Tl(I) and NMR line-narrowing, X-ray diffraction, DTA and electrical conductivity experiments in the case of both the double halides containing Li and the Li tunnel-structure oxides.

Synthesis of Materials and Sample Preparation

Polycrystalline samples of several polycrystalline alkali titanates, germanates and stannates were prepared from high-purity alkali carbonates and TiO_2 , SnO_2 or GeO_2 powders. The powders were mixed in the proper proportions in acetone to yield the desired compound composition, the mixture then being dried, compacted in a die and pre-sintered at $800^\circ\text{--}1000^\circ\text{C}$ for times ranging up to 12 hours. The resulting compact was subsequently crushed and the powder repressed and sintered at $1000^\circ\text{--}1200^\circ\text{C}$ for 1-3 days. Several of the resulting compounds possessed ramsdellite or hollandite structures (rutile-derivative structures) whereas others possessed structures related to that of the tetragonal bronzes. Each of these structures possesses channels in which the alkali ions might be

expected to be highly mobile.

In addition, double halides in the LiCl-MgCl_2 or LiCl-CdCl_2 and the corresponding bromine systems were prepared by mixing the component halides in the proper proportions and fused in a platinum crucible. The resulting polycrystalline samples were subsequently pressed into discs for preliminary electrical conductivity measurements. The initial attempts to prepare single crystals of the double chlorides $(\text{Li}_{1-2x}\text{Cd}_x)\text{Cl}$ and $(\text{Li}_{1-2x}\text{Mg}_x)\text{Cl}$ where $x = 0.33$, utilizing a vacuum furnace and the Czochralski technique, failed. A zone-melting apparatus for the preparation of single crystals of the double halides and the complex In and Tl salts mentioned below has been designed and recently constructed in our machine shop.

The compound In_4CdI_6 was prepared by the reaction of indium metal, iodine and cadmium iodide in an evacuated and sealed pyrex capsule. The capsule was heated above the melting points of all reactants (about 400°C), held at that temperature for 48 h and slowly cooled to room temperature. A brown product resulted whose X-ray powder pattern agreed well with published X-ray data.

The compound Tl_4CdI_6 was also prepared in a similar manner by reacting thallous iodide and cadmium iodide. The thallous iodide, in turn, was prepared by the metathesis reaction between thallous nitrate and potassium iodide. The final product is a gray compound.

Zinc pieces, indium and iodine were reacted in the above manner to prepare the compound In_2ZnI_4 , whereas the compound Tl_2ZnI_4 resulted from the reaction of thallous iodide, iodine and zinc.

Characterization Studies

NMR line narrowing results on the ^7Li resonance line observed between 77° and 500°K on the Li titanates exhibiting the ramsdellite structure and on $(\text{Li}_{0.33}\text{Cd}_{0.33})\text{Cl}$ were encouraging: the ^7Li line was fully narrowed at 300°K in

the case of the compound $\text{Li}_2\text{Ti}_3\text{O}_7$, whereas the resonance line for the double chloride salt narrowed from a width of 2.2G at 91°K to 0.6G at 297°K. These results suggest that there is indeed rapid Li^+ motion in these compounds; unfortunately, the NMR technique cannot differentiate between localized and long-range Li^+ ion transport in these phases and other techniques which probe for Li^+ ion transport must be employed to unambiguously establish that this ionic motion is of a long-range character.

A DTA study of the double chloride systems ($\text{LiCl}-\text{CdCl}_2$ and $\text{LiCl}-\text{MgCl}_2$) gave clear evidence of moisture being driven off at 200-250°C and also showed suggestions of phase changes occurring at temperatures ranging from 250-400°C, depending on the system and the composition. If these double halides are indeed analogous to the superionic conducting Ag double salts (e.g., RbAg_4I_5 and Ag_2HgI_4), one would expect them to exhibit phase transitions with the most highly conductive solid phase occurring in the highest temperature region. Phase diagrams, thermodynamic and structural data are necessary for proper preparation and stability considerations. Towards this end, a high-temperature X-ray diffraction study of these phases has been recently initiated.

Using an ac impedance bridge and Pt electrodes, preliminary electrical conductivity measurements have been made on compacts of the double halide powder pressed pellets. There are also indications in the conductivity data that a change in slope of the conductivity-temperature data does take place at those temperatures where indications of phase changes are found in the DTA results. The room temperature conductivities for these salts ranged from a low value of about $10^{-6} (\Omega\text{cm})^{-1}$ at 300°K to about $10^{-1} (\Omega\text{cm})^{-1}$ at 673°K.

Attempts failed to obtain an estimate of the ionic transference number in the double halides (DH) when cells of the types were used: $\text{LiMg}|\text{DH}|\text{AgI,Ag}$; $\text{Li}|\text{DH}|\text{AgI,Ag}$; $\text{Li}|\text{DH}|\text{Cu}_2\text{S,Cu}$; and $\text{LiAg}|\text{DH}|\text{Cu}_2\text{S,Cu}$. No consistent voltages were

obtained from these cells because of reactions which occurred between the DH electrolyte and some of the electrode materials. Future experiments of this type will be conducted using electrode materials that are found to be compatible with the DH electrolyte at temperatures in the range 200-400°C. Such experiments will be followed up with others utilizing a Wagner polarization cell technique to measure the transference number for electronic charge carriers.

Preliminary ac conductivity measurements on the compound $\text{Li}_2\text{Ti}_3\text{O}_7$ have been attempted using a solution of LiI in propylene carbonate as the reversible electrodes. The activation energy inferred from these data is somewhat higher (0.4eV) than that inferred from NMR line-narrowing results (0.2eV) on the same compound. These conductivity results also show some frequency dependence and have been obtained using samples which exhibit open porosity and are only 75-80% of the theoretical density.

Some preliminary dielectric loss measurements have been done on $\text{Li}_2\text{Ti}_3\text{O}_7$ and the temperature dependence of the Maxwell-Wagner losses observed indicate an activation of approximately 0.4eV, in general agreement with the aforementioned conductivity value.

The Raman spectrum of In_4CdI_6 reveals a number of distinctive peaks: two peaks clearly correspond to CdI_2 and are at frequencies close to those observed for CdI_4^{2-} , while a third peak corresponds to InI . Most importantly, there is no evidence of In(III) in the form of InI_3 which has a strong, distinctive peak. As the temperature is raised, the Raman peaks broaden somewhat and diminish in intensity. Moreover, there is no sudden substantial broadening of the peaks above the reported phase transition temperature even though the transition can be followed visually as the brown compound becomes almost black.

The Raman spectrum of Tl_4CdI_6 reveals peaks attributable to both thallous iodide and cadmium iodide. Upon heating to 215°C, the compound takes on a deeper

gray color and the peaks in the spectrum broaden slightly and lose in intensity. There is no evidence for a polymorphic transition in either the Raman spectrum or in visual observations for color changes.

In the case of In_2ZnI_4 , the Raman spectra showed a peak due to InI_4^- with an intensity about equal to that assignable to ZnI_4^{2-} . Upon passing through the temperature interval 213-222°C (the reported transition temperature is 210°C), the Raman spectrum is dramatically altered as all the peaks except one disappear completely. This remaining peak is quite weak and greatly broadened.

Comparing the Raman spectra of In_2ZnI_4 and Tl_2ZnI_4 and ignoring the peaks due to InI_4^- , both spectra reveal six peaks of similar strength and frequency. Three of these peaks are clearly assignable to ZnI_4^{2-} . The excellent correspondence between the spectra of these two complex compounds suggests that the two structures may be isomorphous.