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New Battery Materials: Final Report

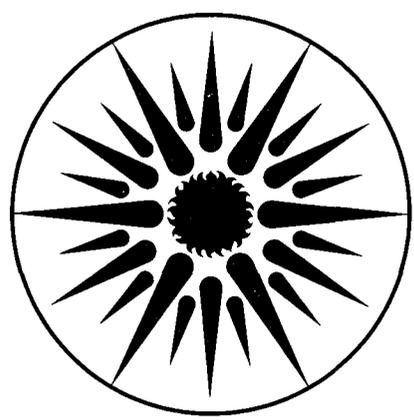R.A. Huggins

March 1989

APPLIED SCIENCE DIVISION

DISCLAIMER

NEW BATTERY MATERIALS

Final Report

March 1989

by

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for

1. Introduction

This program is aimed at the study of materials and phenomena related to advanced battery systems, special attention being given to secondary systems which might be useful for vehicular propulsion or utility load levelling. In particular, the objectives of this program are to understand and evaluate the important structural, thermodynamic and kinetic parameters related to the use of materials as electrolyte or electrode components in high performance secondary battery systems.

In the last year, the exact nature of the individual projects studied under this program has been altered in some respects, while the overall objectives of the program have remained unchanged. In particular, previous projects involving the characterisation of negative electrode components for use in lithum batteries, positive electrode components in the Li - Mo - O system for use in lithium batteries, and glassy lithium electrolytes in the Li - Si - S system have been completed and discontinued.

The work undertaken during the last year falls into several categories. What follows is a report of our activities in some of these research areas. These include: the study of negative electrode materials for use in reversible sodium-based systems; the study of novel electrolyte systems for use in reversible sodium-based batteries; and the use of atmospheric pressure chemical vapor deposition for the preparation of thin film battery components. These will now be considered in turn. Several publications have resulted from this work, and are listed in the Appendix.

2. The "Zebra" cell concept

The sodium cell-related work referred to in the Introduction is concerned primarily with the investigation of possible modifications and improvements of the "Zebra" cell concept. This relatively new type of battery system concept is described briefly here.

Recently, the "Zebra cell" concept has attracted attention as a possible alternative to the sodium-sulfur cell for use in high power / specific energy applications, e.g. for vehicle propulsion or load-levelling. The Zebra cell is a low temperature (approximately 250° C) sodium-based cell of the form

$$(-)\ Na\ (l)\ /\ Na\ ß''-Al_2O_3\ (s)\ /\ NaAlCl_4\ (l)\ /\ MCl_2\ (s)\ (+)$$
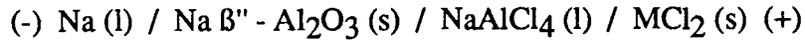
where M represents Fe or Ni. When $NiCl_2$ is used as the positive electrode, the term "Cheetah cell" has been employed to describe the system, although the general term "Zebra cell" will be used here to describe all cells of the above type.

The Zebra cell is a Na / MCl_2 cell in which the sodium is transported through two electrolytes, one solid and one liquid, in series, the overall cell reaction being

$$MCl_2\ +\ 2\ Na\ =\ M\ +\ 2\ NaCl$$
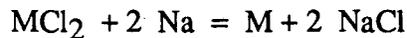
leading to open-circuit cell voltages of 2.35 V and 2.59 V at 250° C for M = Fe and Ni, respectively, with capacities of 2 Na/M. These cells have high theoretical specific energies: 503 and 545 Wh/kg for M = Fe and Ni, respectively. In the case of M = Fe, it has been reported that ternary phase formation occurs during discharge, via the solid state displacement of metallic iron,

$$6\ Na\ +\ 4\ FeCl_2\ =\ Na_6FeCl_8\ +\ 3\ Fe$$

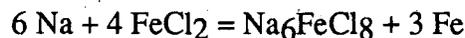although this appears to have only a negligible effect on the operating cell voltage. This effect appears to be absent when M = Ni. Further, cells which employ $NiCl_2$ as the positive electrode appear to have a higher power capability than those using $FeCl_2$. The simple cell reactions described above mean that cells may be assembled in a fully discharged state, i.e. requiring only inexpensive elemental Fe or Ni and salt as the initial positive electrode components. The Na ß'' - Al_2O_3 electrolyte component is necessary since $NaAlCl_4$ is not stable in contact with sodium, as was shown by work in this laboratory some time ago. Although, in principle, Zebra cells may be operated in the temperature range 150 - 400° C, the resistivity of the ß'' - Al_2O_3 component forces the operating temperature to be at least 250° C. This point will be returned to below.

The Zebra cell has several important advantages over the Na / S cell:

a. The use of a chloride, rather than sulfide, positive electrode eliminates sulfur-related corrosion problems.

b. The cell reaction is less exothermic, leading to greater battery reliability and safety.

c. $NaAlCl_4$ melts at approximately 150° C; this means that Zebra cells may be operated at a lower temperature than is possible in the Na / S system, which is limited by features of the Na-S phase diagram.

d. The Zebra cell operating voltage is somewhat higher than that found in the Na / S cell.

e. The Zebra cell chemistry leads to overcharge and overdischarge protection mechanisms.

2.1 Possible negative electrode / electrolyte modifications

Despite the promising characteristics of the Zebra cell described above, it is apparent that certain improvements would be desirable. The most important concerns the replacement of the Na ß" - Al_2O_3 solid electrolyte component which:

a. adds significantly to the overall cell resistance while adding weight,

b. in common with many ceramic systems, is difficult to fabricate into arbitrary shapes,

c. has poor mechanical stability,

d. may have long term electrochemical stability problems at high sodium activities, and

e. may cause long-term cell stability problems due to de-wetting.

Removal of the solid electrolyte component dictates that a replacement for the molten sodium / Na ß" - Al_2O_3 / $NaAlCl_4$ combination would have to be found. At its simplest, this could involve a high sodium activity sodium alloy and a liquid electrolyte (e.g. a low melting molten salt). During the past year, we have been engaged in a preliminary search for possible sodium alloy negative electrodes, and the results are described in Section 3.

Any replacement molten salt electrolyte must satisfy two basic criteria: first, it must be stable from approximately 0 to at least 2.5 V vs. sodium. Second, it must have a melting point in the range 100 - 250° C. At the present time, two system types appear to be promising candidates:

a. Sodium salt ammoniates.

Relatively recently it has become apparent that some low melting ammoniates of various sodium (and lithium) salts do not dissolve or react with the relevant alkali metal and possess low ammonia pressures in the temperature range 25 - 200° C (1,2). Further, some of these materials appear to have relatively large electrochemical stability windows, in the range 0 - 2.5 V vs. the alkali metal, and high conductivities for the alkali metal ions. To date, only the ammoniates of NaI and LiClO$_4$ have received extensive study, and only in the vicinity of room temperature. It should be emphasized that it is not intended to pursue the study of perchlorate-based systems in this work; they are described here only for comparison with the NaI-based system. The compositions, ammonia vapor pressures, densities and, where available, conductivities of the two series of ammoniates are given in Table 1. It is evident from the data in Table 1 that, of the limited number of compositions studied thus far, the NaI-derived electrolytes, which are liquid at room temperature when the ammonia to NaI ratio is in the range 3 to 4.5, appear to have favorable physical properties for the use intended here. Further, they are less viscous than those derived from LiClO$_4$. Figure 1 shows the variation of conductivity, calculated from high frequency impedance data (1), with reciprocal temperature for two compositions in the NaI-based system: NaI·3NH$_3$, which is a liquid at the temperatures covered in Figure 1, and NaI·3.5NH$_3$, which is a gel. Two features are evident from Figure 1. First, the sodium ion conductivities of both compositions are relatively high at these temperatures and, second, the gel conductivity is only slightly less than that of the liquid. It has been reported that gel formation, as well as occurring as a function of composition, will also occur on cooling the liquid ammoniates. The formation of a high-conductivity gel on cooling has an important consequence for battery operation, i.e. that accidental freezing of the electrolyte component during the operation of a cell will not cause a significant increase in cell impedance and, further, will not result in the development of unacceptably high stresses. These electrolytes have been tested with a number of Na (or Li) / positive electrode couples, as shown in Table 2. On short-circuit, such cells exhibit current densities of the order of 1 A cm^{-2}. Although relatively little is known at the present time about the behavior of these ammoniate electrolytes at high positive potentials, it may be expected that iodine vapor evolution will occur when the positive stability limit of a NaI-based

Table 1. Physical Properties of Some Alkali Metal Salt Ammoniates at 20 °C

Composition	Vapor pressure / cm Hg	Density / g cm^{-3}	Conductivity / Ω^{-1} cm^{-1}
NaI. 3NH$_3$	37	1.63	0.14
NaI. 3.3NH$_3$	43	1.58	0.14
NaI. 3.6NH$_3$	55	1.54	0.11
LiClO$_4$. 3.4NH$_3$	73	1.2	- - - -
LiClO$_4$. 4NH$_3$	75	1.2	0.03
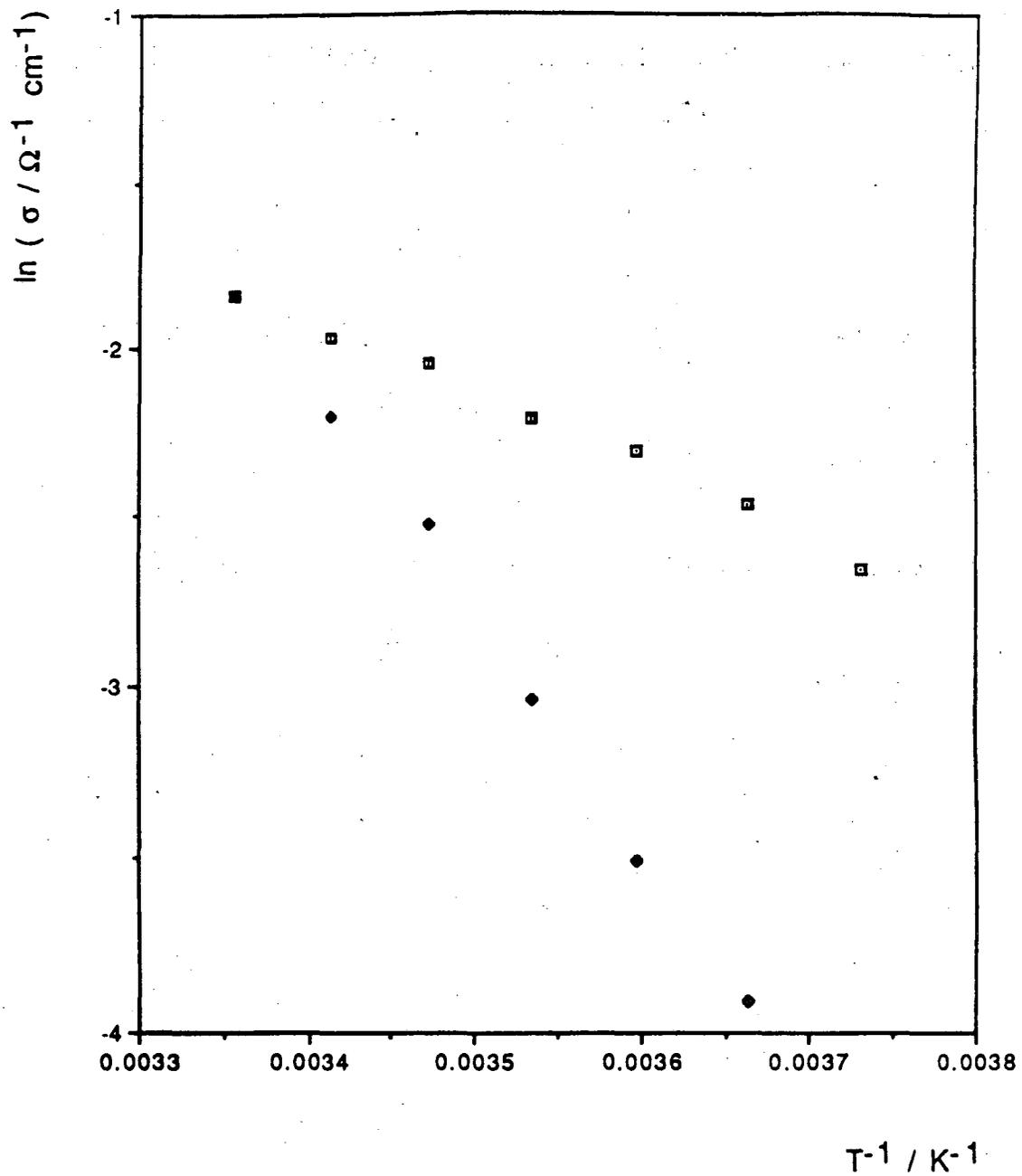
Fig. 1   Variation of conductivity with reciprocal temperature for NaI.3NH$_3$ liquid (upper curve) and NaI.3.5NH$_3$ gel (lower curve).

Table 2. Open-circuit cell voltages at 20 °C

Electrolyte	Couple	Voltage / V
$NaI.3.3NH_3$	$Na / (Sn)_x$	2.4
"	Na / MnO_2	2.5
"	$Na / Cu_4O(PO_4)_2$	2.5
"	Na / CuO	2.2
$LiClO_4. 4NH_3$	$Li / (Sn)_x$	2.8
"	Li / MnO_2	2.9
"	$Li / Cu_4O(PO_4)_2$	2.9
"	Li / CuO	2.6

ammoniate is exceeded. This provides a convenient overcharge protection mechanism, via iodine evolution and subsequent transport to the negative electrode.

The results of our studies on the initial characterization of such ammoniate electrolytes for use in Zebra-type cells are given in Section 4.

b. Organometallic electrolytes.

These are described briefly in Section 3.

3. Sodium-based negative electrode materials

A significant portion of the work carried out under this program in recent years has been concentrated on developing both practical and theoretical methodologies for finding alloy-based alternatives to pure lithium for use as negative electrode materials in reversible lithium batteries. Significant progress has been made in this regard; several lithium alloy systems have been shown to possess excellent electrochemical properties when used as negative electrodes. Further, these electrochemical properties have received detailed thermodynamic and kinetic rationalization. With this background, we have shifted our attention in this area to the investigation of analogous sodium-based alloy systems. This has been undertaken primarily in order to develop alternative negative electrode assemblies for use in the "Zebra cell" class of reversible, high-rate, intermediate temperature sodium-based cells. The background to this area of study, and rationale behind the search for alternative negative materials, is discussed in detail in Section 2 of this report.

Of key importance in determining the potential advantages possessed by a candidate alloy system as an electrode material is the relevant isothermal phase diagram. Previous experience has led us to believe that existing alloy phase diagrams, which are conventionally determined at high temperatures, may not, in some cases, be relied upon when extrapolated to somewhat lower temperatures. Hence, in order to obtain preliminary thermodynamic information for these candidate alloy systems, we have employed simple cells of the type

$$(-) \ Na \ (l) \ / \ NaAlEt_4 \ (l) \ / \ sodium \ alloy \ (s) \ (+)$$
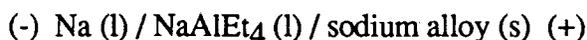
which operate at approximately 110° C. An interesting feature of this type of cell is the use of an organometallic, low-melting electrolyte. Previously, we have demonstrated that the low-melting (110° C) salt $NaAlEt_4$ (Et = ethyl) is stable in contact with elemental sodium and at positive potentials up to approximately 1 V vs. Na, i.e. over the range covered by any candidate alloy electrode system.

A number of alloy compositions have been screened for their ability to act as fast, reversible sodium-conducting electrodes. In contrast to our experience with lithium-based systems, only a relatively limited number of sodium alloy systems appeared suitable in this respect. These are described here. The variation of open-circuit voltage with composition for a number of compositions within the Na - Pb, Na - Sn and Na - Bi systems are shown in Figures 2, 3 and 4. These results may be viewed as simple isothermal two - component phase diagrams where, most importantly, regions of composition-independent voltage indicate the presence of two phases. The results for the Na-Pb system show the existence of four single phase regions at this temperature, with nominal compositions Na_2Pb_5, NaPb, Na_2Pb and Na_4Pb. The two-phase region between "Na_2Pb" and "Na_4Pb" represents a particularly attractive low-potential plateau (at approx. 100 mV vs. Na) with a capacity of 2 Na / Pb. The variation of operating cell voltage with current density during discharging and charging of compositions on this plateau is shown in Figure 5. The Na-Sn system also contains a plateau at approx. 100 mV vs. Na, but with a capacity of only 1 Na / Sn. The diffusion of Na in the Na-Bi system is observed to be particularly fast; however, as seen in Figure 4, a suitable low potential plateau is not present over the composition range studied here.

4. Preparation and characterization of alkali halide ammoniate electrolytes for use in sodium-based systems

As explained above, the elimination of the ceramic electrolyte component from the Zebra cell configuration entails the use of a new molten salt electrolyte which is stable over the range 0 - 2.5 V vs. Na. Recently, we have studied the potential exploitation of a family of alkali halide ammoniate salts of the form $MX \cdot nNH_3$ where MX is an alkali halide. These salts are either liquid at room temperature or have relatively low melting points. Further, they have been reported to have high alkali metal ion conductivities (1,2).

Fig. 2   Variation of open-circuit cell voltage (vs. Na) with composition for the Na-Pb system.
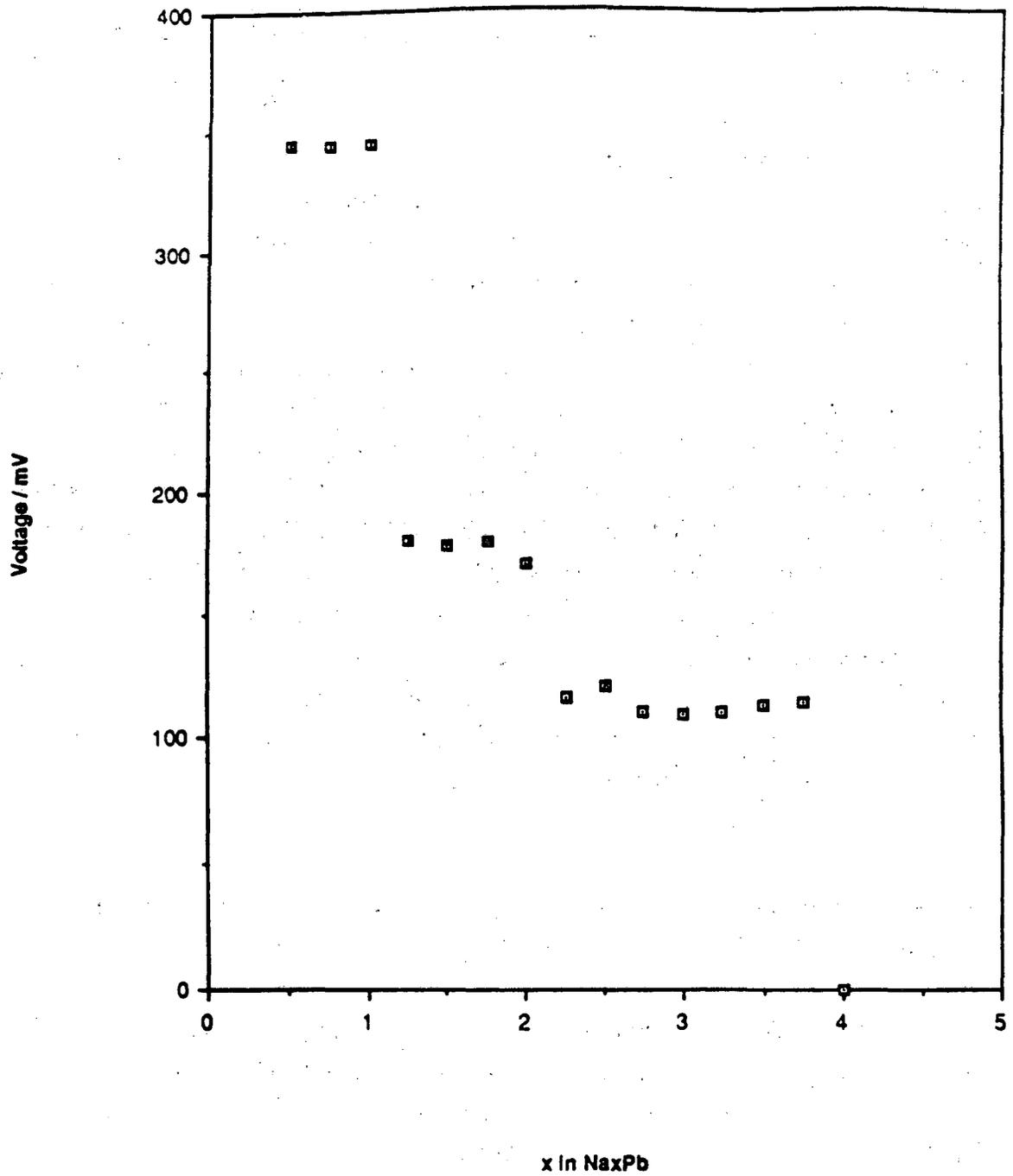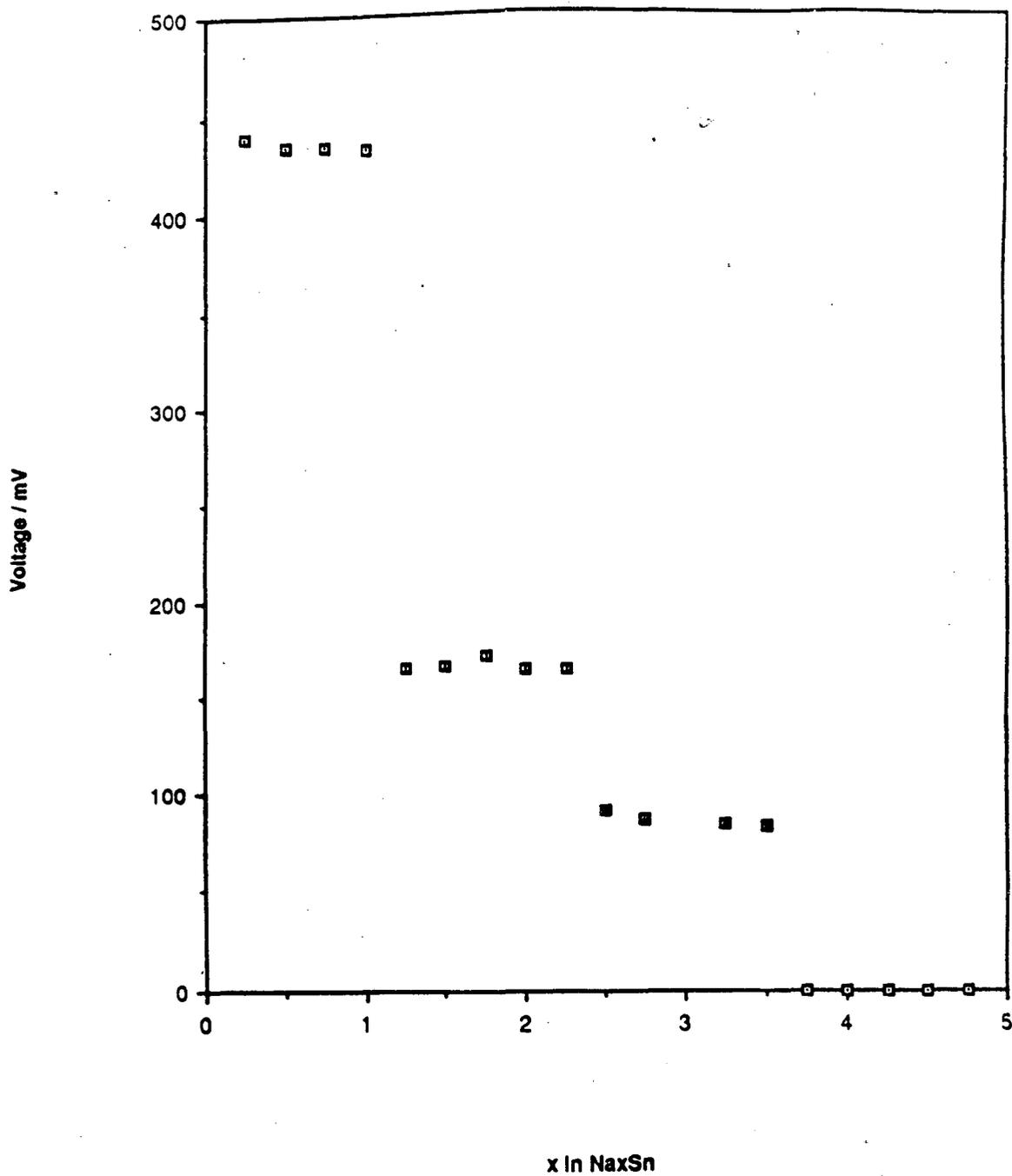
Fig. 3   Variation of open-circuit cell voltage (vs. Na) with composition for the Na-Sn system.
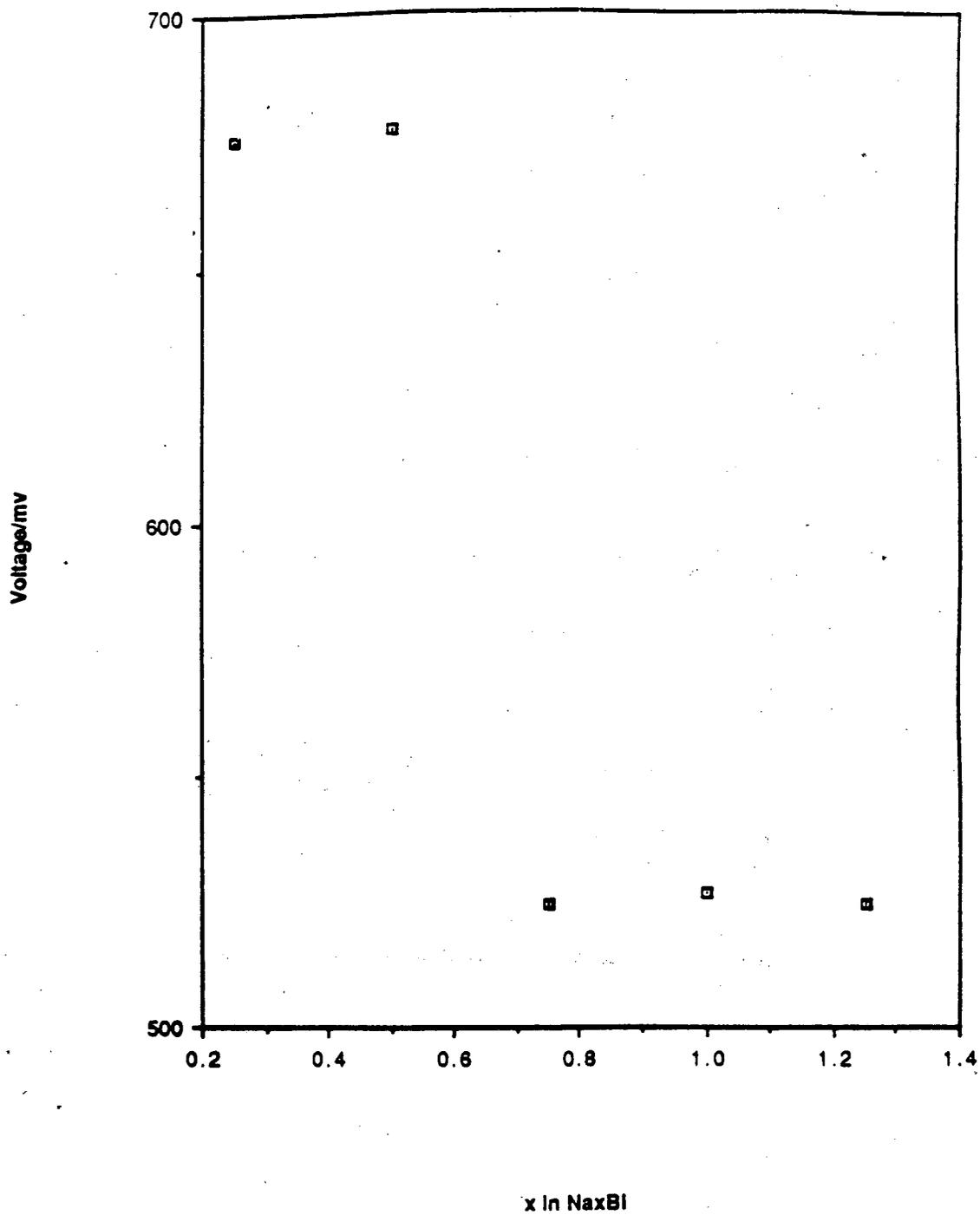
Fig. 4   Variation of open-circuit cell voltage (vs. Na) with composition for the Na-Bi system.
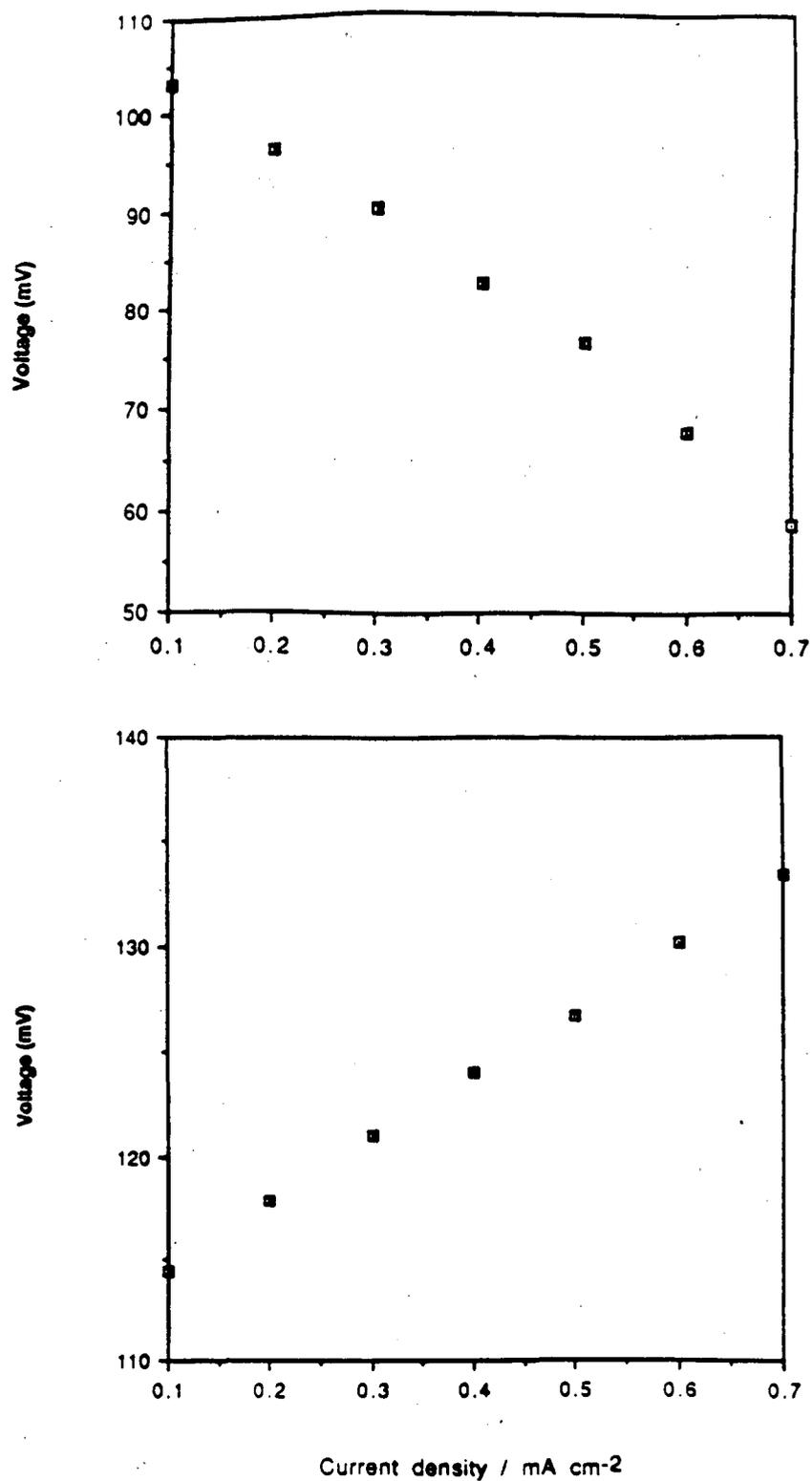
Fig. 5   Variation of operating cell voltage (vs. Na) with current density for discharge (upper curve) and charge (lower curve) of compositions on 100 mV plateau in Na-Pb system.

4.1 Preparation and characterization of NaI·4.5NH3

One of the most straightforward of the alkali halide ammoniate compositions to study is NaI·4.5NH3 since it is a liquid at room temperature. Consequently, this composition was chosen as a model system for initial study of the electrochemical properties of such materials. Samples of NaI·4.5NH3 were prepared by passing gaseous ammonia over thoroughly dried NaI at 0° C. The ammoniate is formed as a colorless, relatively non-viscous liquid.

Contrary to earlier reports in the literature (1,2), it was observed that NaI·4.5NH3 was not stable in the presence of either elemental sodium or lithium. In both cases reaction occurred leading to the formation of white insoluble products with vigorous bubbling. A cell of the form:

$$(-) \text{ Mo / NaI·4.5NH}_3 \text{ / Mo } (+)$$
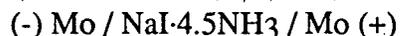
was constructed and the current density in the cell measured as a function of applied voltage. Typical results are reported in Figure 6. It is apparent that decomposition of the electrolyte begins at an applied voltage of approximately 2.6 V. A voltage stability window in this range indicates that the electrolyte is potentially useful. However, the position of this window relative to a reference potential, that of elemental sodium in this case, must also be determined.

The calculated Na - N - H phase diagram at room temperature is shown in Figure 7. This indicates that sodium will react with ammonia (at unit activity) at a potential of 0.49 V vs. Na to form hydrogen and sodamide. Although the activity of ammonia in the molten electrolyte is not unity, the measured vapor pressure of NaI·4.5NH3 is of the order of 30 cm Hg which will cause a negligible difference in the measured and calculated decomposition potentials. Hence, we may assume that the negative electrode decomposition reaction is of the form:

$$\text{NaI·4.5NH}_3 + 4.5 \text{ Na}^+ + 4.5 \text{ e}^- = 4.5 \text{ NaNH}_2 + \text{NaI} + 2.25 \text{ H}_2 \quad E = 0.49 \text{ V vs. Na}$$

Using the measured value of the standard molar Gibbs free energy of formation of NaI·4.5NH3, we may calculate the partial quaternary Na - N - H - I phase diagram at room temperature, Figure 8. This predicts that the positive electrode decomposition reaction will be:
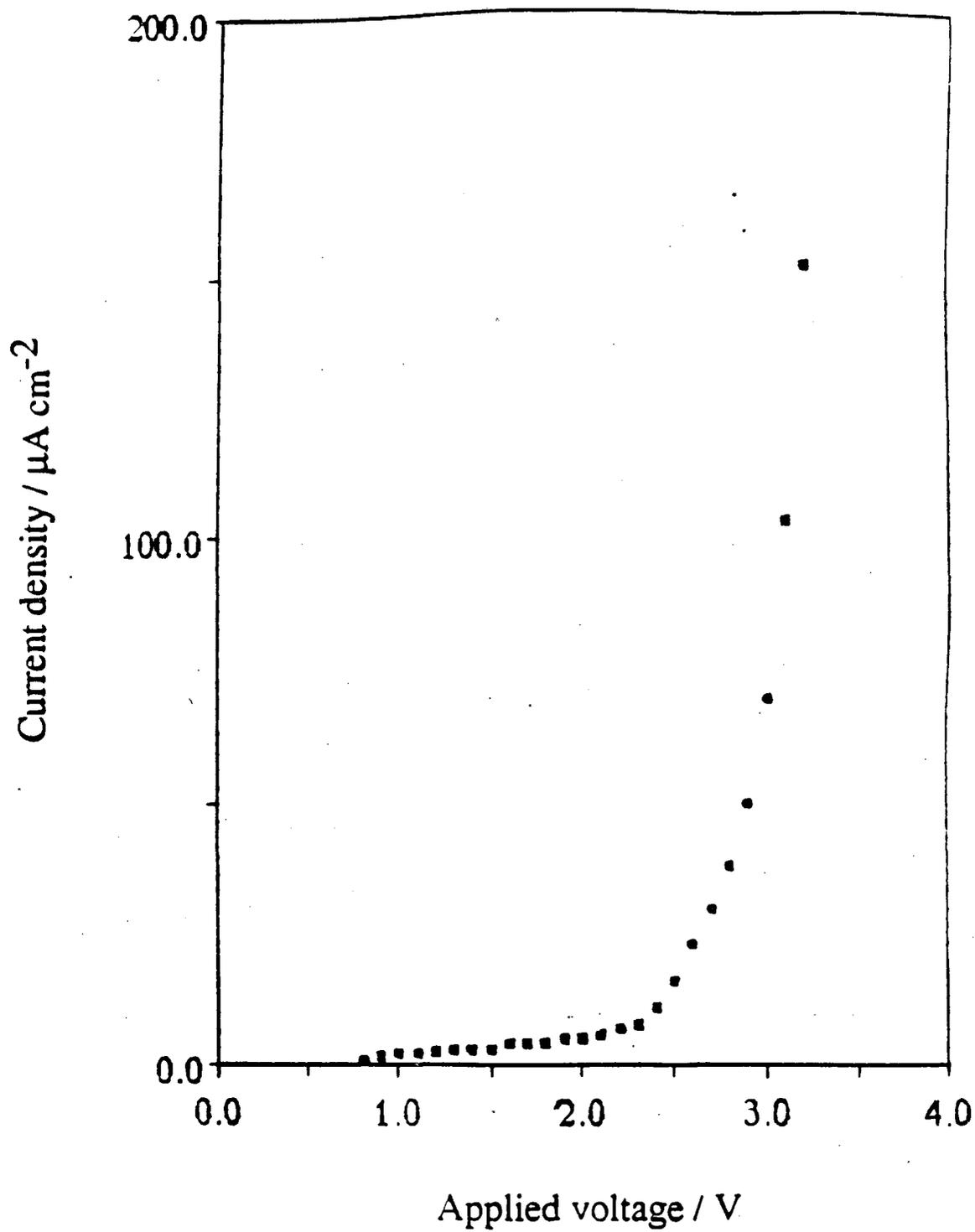
$$\text{NaI·4.5NH}_3 = \text{Na}^+ + \text{e}^- + 4.5 \text{ NH}_3 + 0.5 \text{ I}_2 \quad E = 3.03 \text{ V vs. Na}$$
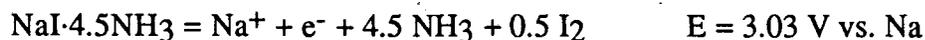
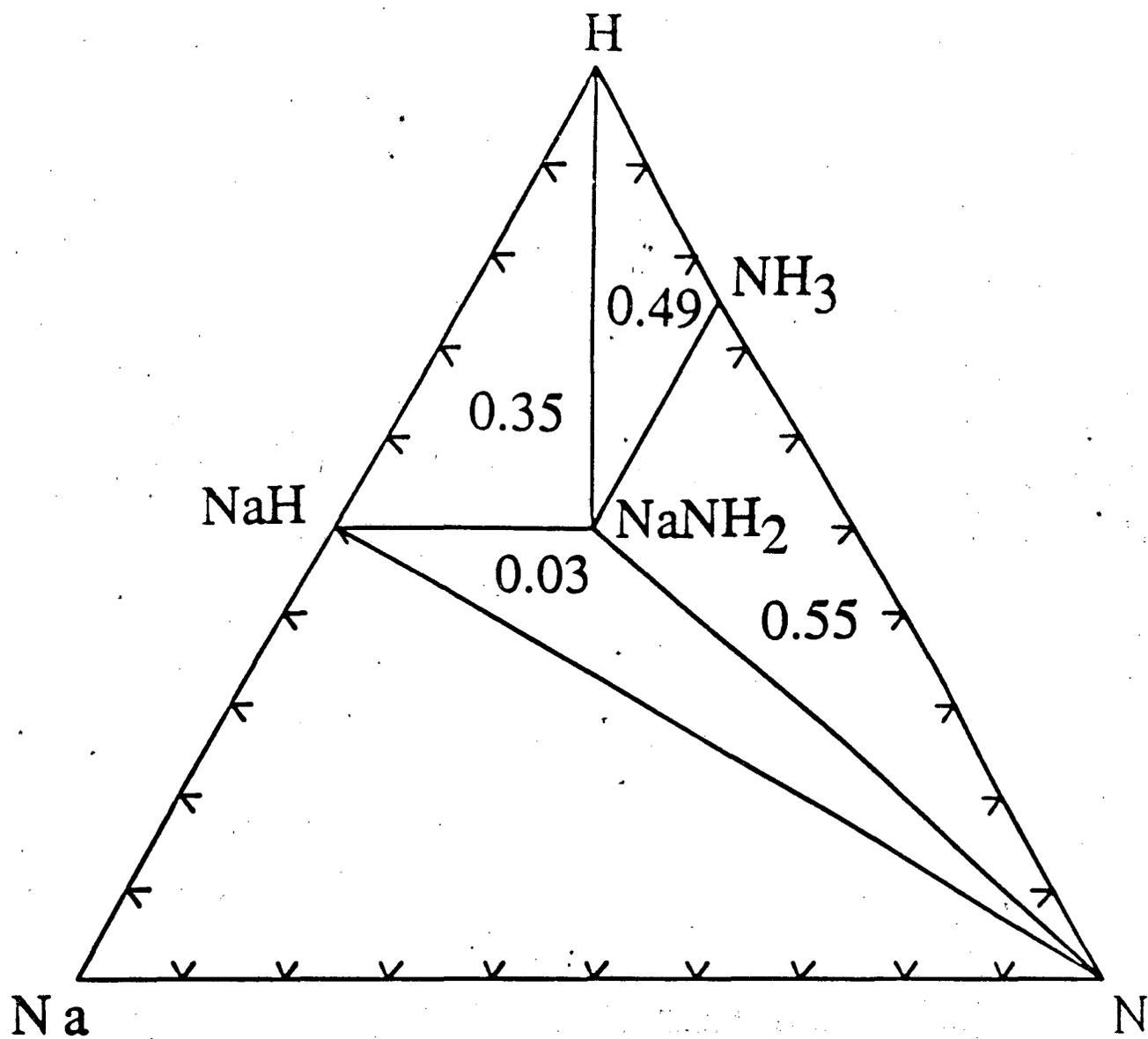Fig. 6.   NaI · 4.5 NH$_3$, 298°K.
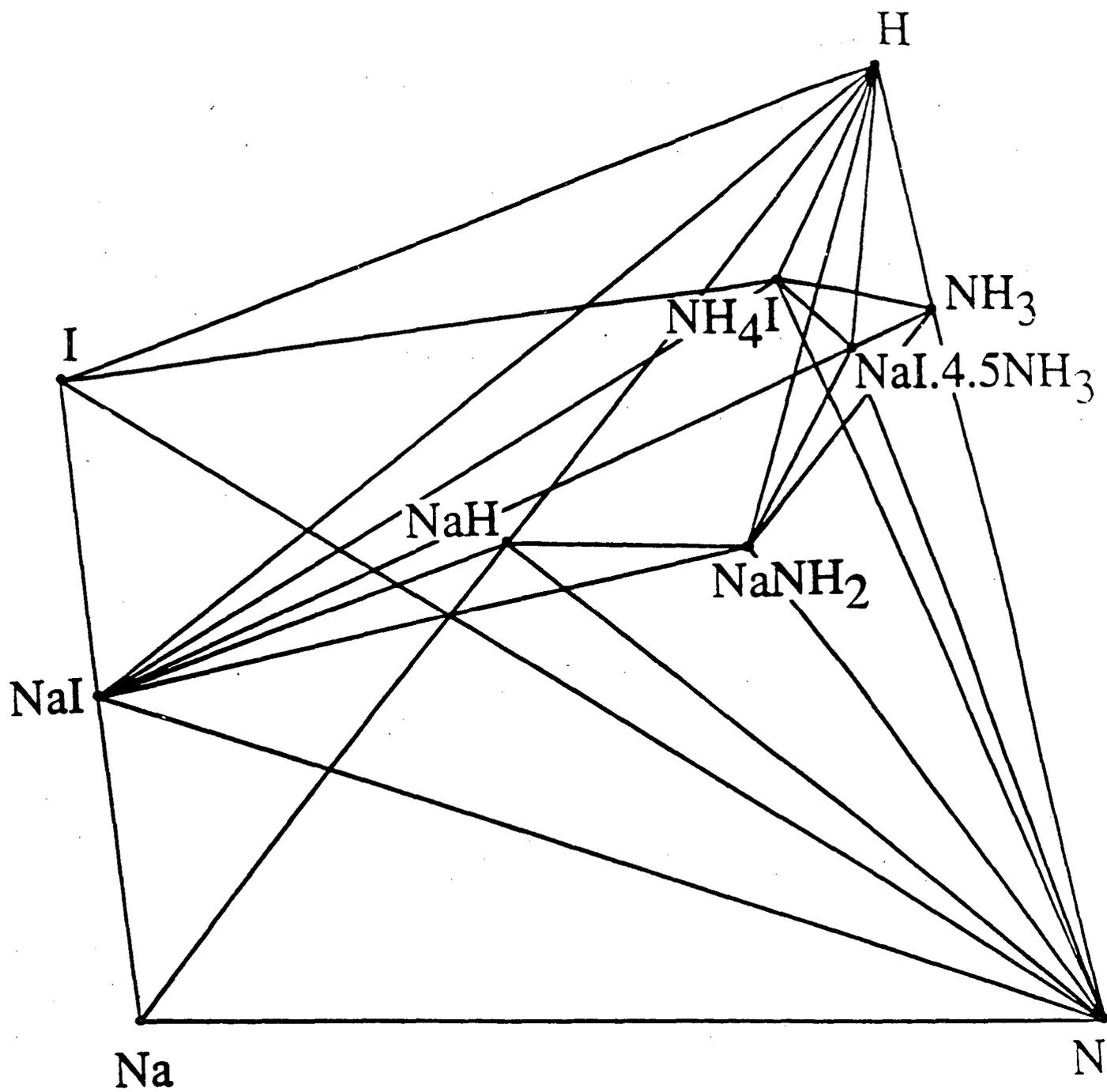
Fig. 7.　Na—N—H, 298°K.

Fig. 8.   Na—N—H—I phase diagram, 298°K.

Hence, the decomposition voltage for the ammoniate electrolyte is predicted to be 2.56 V using inert electrodes, in excellent agreement with the experimentally observed value. The decomposition potentials calculated here support our experimental finding that, contrary to earlier reports (1,2), the alkali halide ammoniate studied here is not stable in the presence of elemental sodium. It is, however, stable to a relatively high positive potential, one ideally suited to match the values employed in the Zebra cell. As described above, Section 3, we have measured the electrical properties of some sodium alloy systems which have potential use as negative electrode components in Zebra cell type arrangements. Some of these systems, in particular Na - Bi and Na - Sb, possess coulometric titration curves with constant voltage plateaus at potentials slightly higher than 0.5 V vs. Na. Although plateau voltages of this magnitude may not be suitable for use in systems where the electrolyte is stable to very low potentials vs. Na, they are compatible for use with the ammoniate electrolyte.

Our current work is focussed on the further characterization of some ammoniate electrolyte systems, together with the construction and testing of sodium-based cells which employ these electrolytes together with thermodynamically compatible electrode components in a Zebra cell type arrangement.

5. Preparation of thin-film electrode and electrolyte materials using the atmospheric pressure chemical vapor deposition method

One of the critical features that will determine the feasibility of the development of very large surface/volume ratio electrochemical cells for high power applications will be the method used for the fabrication of thin layers or multilayer configurations. Most of the techniques that have been employed for the production of multi-micron scale films or layers are inherently slow or expensive. An exception to this is the continuous moving belt high rate atmospheric pressure chemical vapor deposition technique, using equipment of the type currently produced by the Watkins-Johnson Co., who developed this type of high-rate deposition equipment. While presently being used commercially (primarily in Japan) for the preparation of silicon and tin oxides, such an approach is ideally suited to the continuous, high rate deposition of thin layers of advanced battery components. The atmospheric pressure chemical vapor deposition technique being explored involves the use of a continuous belt carrying the desired substrate moving under a carefully designed gas injector with parallel laminar flow gas streams separated by a third stream of an inert gas to prevent reaction before arrival upon the substrate surface.

By the use of a series of muffle obstructions and blanket gas curtains with controlled pressure differences, it has been shown to be possible to almost completely restrict the ingress of air from the outside. Impressive uniform and defect-free films have been made of a number of highly reactive materials under continuous conditions at temperatures well below their melting points with this type of equipment. A special small scale mock-up of the critical parts of the apparatus described above has been engineered and constructed for use in our laboratory by the Watkins-Johnson Co.

An initial evaluation has been made of the following two battery cathode materials: iron sulfide and manganese oxide. The results to date include production of thin films of each material by CVD, examination by SEM, and analysis by X-ray diffraction and electron microprobe methods. Electrochemical studies are underway to determine both the dynamic potentials and the OCV potentials of each material at room temperature in a battery configuration using pure Li as the anode. The results are discussed in the following sections:

5.1 Iron sulfide

Thin films of iron sulfide of varying stoichiometry have been deposited on glass, aluminum or molybdenum substrates by reacting iron pentacarbonyl and H_2S in our atmospheric pressure CVD apparatus. Nitrogen was used as a carrier gas for the $Fe(CO)_5$. The deposition thickness was found to vary linearly with time and flow rate. By varying the ratio of the reactants, the composition of the deposit could be varied from $Fe_{53}S_{47}$ to $Fe_{33}S_{67}$. Examination by SEM showed that the films varied from a smooth, compact layer to a rough, granular layer. The reason for the different morphologies has not been identified. The compact film is apparently more prone to cracking and spalling from the substrate than the granular film. The deposition temperature was also varied from 150 to 450° C. Low temperatures (150 - 200° C) gave poor deposition rates whereas higher temperatures (above 300° C) gave amorphous deposits as well as low deposition rates. The optimum deposition temperature was found to be 250° C. Under these conditions, X-ray analysis indicated that the as-deposited film possessed the marcasite (orthorhombic) structure. The color of the films varied from silver-grey to black and the deposits had a reflective, mirror-like surface. Films deposited above 350° C had a yellow-gold color and were translucent.

Samples of iron sulfide on aluminum or molybdenum foil were tested as positive electrode materials in an electrochemical cell with a Li negative electrode and an electrolyte consisting of $LiAsF_6$ dissolved in propylene carbonate, i.e. in cells of the form:

$$(-) \; Li \, / \, LiAsF_6 \; (in \; PC) \, / \, FeS_x \; (x = 1.5) \; (+)$$

The results of preliminary experiments indicate that such films may be discharged at current densities up to 0.1 mA cm^{-2} with minimal electrode polarization. Further, a constant-voltage plateau is observed at approximately 1.7 V vs. Li with a capacity in excess of 1 Li per FeS_x. The high-temperature amorphous films showed poor discharge characteristics with no constant-voltage plateau evident. the 250°C deposits performed much better. Discharge at 10 µA cm^{-2} yielded a 1.6 V plateau, whereas discharge at 100 µA cm^{-2} gave a 1.4 V plateau. At higher current densities, the voltage deteriorated continuously and no plateau was found. Attempts at recharging resulted in high overpotentials, possibly due to delamination of the deposit from the substrate. These room-temperature results indicate that the iron sulfide films deposited here may be useful for application in the intermediate-temperature Li/FeS_2 batteries under study elsewhere.

In a hypothetical battery design for use at room temperature, CVD-produced films of iron sulfide could be spiral wound with the anode and electrolyte wrapped in a sandwich construction. A typical C-cell battery has useful dimensions of 2 cm diameter by 4 cm high. If each layer is 100 mm thick, then 100 layers could be wrapped in each cell, giving a total surface area of 2500 cm^2. Such a battery could deliver a current density of 100 µA/cm^2 or a total current of 250 mA.

5.2 Manganese oxide.

Manganese dioxide is commonly used in alkaline $Zn \, / \, KOH \, / \, MnO_2$ batteries while secondary $Zn \, / \, MnO_2$ batteries are under development in the U. S. and Austria. More recently, MnO_2 and other ternary lithium - manganese - oxide phases have been used as positive electrode materials in commercial primary (and experimental secondary) lithium-based batteries employing non-aqueous electrolytes. There is currently significant interest in Japan in the exploitation of this type of secondary cell. In view of this, we have decided to investigate the deposition of thin films of various manganese oxide phases by atmospheric pressure chemical vapor deposition and their subsequent behavior in lithium-based battery systems.

As described above, we have reported the successful production of thin films of FeS_x ($1 < x < 2$) using $Fe(CO)_5$ as one source material. The manganese analog of $Fe(CO)_5$ is $Mn_2(CO)_{10}$ but this is an unstable solid which is readily decomposed by air, water and heat. Our organometallic manganese source was methylcyclopentadienyl manganese tricarbonyl ($CH_3C_5H_4Mn(CO)_3$) obtained from Aldrich Chemical Company. It is a relatively stable liquid, developed as a gasoline additive to replace lead. This material has a 97% purity and is readily available at low cost. It has a m.p. of -1°C and a b.p. of 232° C but there are no data available on vapor pressure or decomposition temperature. We were unable to find any published work on the deposition of MnO_2 thin films, although Mn-doped ZnS films have been produced by CVD using the same manganese source. Using pure O_2 as the oxidizer, initial results were poor, with only slight coloration of the glass substrate. After several runs, we had determined that the following factors were critical in forming a deposit of 1 μm thickness or more:

a. The substrate temperature must be at least 400° C. We chose 450° C as the standard for our experiments. Above 500° C, the deposition rate reaches a plateau, indicating complete cracking of the organometallic manganese complex. Therefore, 450 - 500° C appears to be the optimum temperature of operation.

b. The bubbler must be heated to raise the vapor pressure of yhe organometallic source. In the previous work on Mn-doped ZnS it was reported that an order-of-magnitude increase in deposition rate was obtained by raising the temperature of the bubbler from 50 to 120° C. We set the bubbler temperature at 110 - 120° C.

c. A flow rate of at least 100 cm^3/min of nitrogen through the bubbler is required. Lower flow rates will require much longer exposure times. Our flow rates were varied from 50 to 400 cm^3/min.

d. We found a minimum exposure time of 40 min was required in order to obtain a measurable deposit. Deposition thickness increased with time thereafter.

The composition of the films deposited under the above conditions was found to be Mn_3O_4 (hausmanite), as determined by powder X-ray diffraction. Further, the nature of the oxidizer (pure O_2, CO_2, or 3 ppm O_2 in N_2) was found to have no effect on the composition of the film. The morphology of the manganese oxide films was also different from that of the FeS_x films obtained previously. The Mn_3O_4 had a dull, powdery texture that could easily be brushed off the substrate. Microscopic examination revealed a deposit consisting of globules 0.2 - 1.0 mm in size. The presence of the globules, the lack of adhesion to the substrate, and the delayed start of deposition indicate probable entrainment of liquid in the carrier gas and

possible vapor-phase reaction during the CVD process. Further work will need to focus on a solution to these problems. This may require an alternate source of manganese.

Electrochemical tests showed that this material was not suitable as a battery cathode at room temperature. This may well have been due to the morphology of the films since, at least at intermediate temperatures, Mn_3O_4 is known to behave well in lithium-based cells.

References

1. J. Badoz - Lambling et al, J. Electrochem. Soc. <u>135</u>, 587 (1988).
2. J. Badoz et al, U. S. Patent, 4446215 (1984).

APPENDIX

Publications and Presentations Related to This Program.

1. 1987 and 1988 Publications Related to This Program

A. Anani, S. Crouch-Baker and R.A. Huggins, "Kinetic and Thermodynamic Parameters of Several Binary Lithium Alloy Negative Electrode Materials at Ambient Temperature", J. Electrochem. Soc. 134, 3098 (1987).

C-K. Huang, S. Crouch-Baker and R. A. Huggins, "Lithium Insertion in Several Molybdenum (IV) Oxide Phases at Room Temperature", J. Electrochem. Soc. 135, 408 (1988).

R.A. Huggins, "Polyphase Alloys as Rechargeable Electrodes in Advanced Battery Systems", in Space Electrochemical Research Technology, NASA Conference Publication 2484, (1987), p. 179; and J. Power Sources 22, 341 (1988).

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B. T. Ahn, "Solid State Ionics: Studies of Lithium-Conducting Glasses and A Superconducting Oxide Compound", PhD. dissertation.

2. 1987 and 1988 Presentations Related to This Program

R.A. Huggins, "New Battery Materials", presented at the 8th Battery and Electrochemical Contractors' Conference, Washington, November, 1987.

R.A. Huggins, "Solid State Ionics", presented at the meeting of the Materials Research Society, Reno, April, 1988.

R.A. Huggins, "Some Aspects of Ionic Conductors", presented at the MRS International Meeting on Advanced Materials, Tokyo, May, 1988.

R.A. Huggins, "Materials Science Principles Related to Alloys of Potential Use in Rechargeable Lithium Cells", presented at the 4th International Meeting on Lithium Batteries, Vancouver, BC, May, 1988.

A. Petric, S. Crouch-Baker, R. M. Emerson, T. M. Gür and R. A. Huggins, "Thin Film Positive Electrodes for Lithium-Iron Sulfide Batteries Produced by Atmospheric Pressure Chemical Vapor Deposition", presented at the 174th Meeting of the Electrochemical Society, Chicago, October 9-14, 1988.

S. Crouch-Baker and R. A. Huggins, "Composite Polyphase Electrochemical Cell Components", presented at the Fall Meeting of the Materials Research Society, Boston, November 28-December 3, 1988.

3. Manuscripts and Abstracts Accepted and Submitted Related to This Program

Robert A. Huggins, "Materials Science Principles Related to Alloys of Potential Use in Rechargeable Lithium Cells", to be published in the Journal of Power Sources.

Robert A. Huggins, "Future Expectations for the Application of Solid Ionic Conductors", to be published in High Conductivity Solid Ionic Conductors: Recent Trends and Applications, ed. by T. Takahashi, World Scientific Publishing Company.

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