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"NOVEL CONCEPTS IN ELECTROCHEMICAL SOLAR CELLS"

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I. INTRODUCTION

This report contains a synopsis of the work achieved to date and currently in hand for the Technical Contract No. 3951 with the Solar Energy Research Institute.

Initially, our emphasis has been directed toward the development and evaluation of an efficient, operational photoelectrochemical cell (PEC) system involving (i) molten salt (and/or highly concentrated, inorganic, non-aqueous) electrolytes, and (ii) the promising semiconductor electrode materials such as CuInS_2 , CuInSe_2 , MoS_2 , MoSe_2 etc. As a direct consequence, the stages of the work program that are most critical at this time are the electrode fabrication and characterization and the electrolyte preparation and characterization phases.

Two papers dealing primarily with electrode (n-GaAs) performance have been prepared for publication and drafts of these are enclosed in the Appendix of this report [1,2]. Their contents will be discussed further in the appropriate sections below.

II. RESULTS

II.1 Preparation and Characterization of Electrolytes

II.1.1 Molten Salt Studies

The electrolyte with which we have had most experience to date is the ambient temperature ionic liquid comprising varying molar ratios of aluminum chloride and 1-butylpyridinium chloride. Dr. R. J. Gale, who has had considerable experience handling this electrolyte system and with electrochemical methods in general, has joined this project. The physical and electrochemical properties of this electrolyte system have been characterized fairly extensively by the research groups of Dr. R. A. Osteryoung (CSU and NY State University at Buffalo) [3-7] and Dr. L. A. King and coworkers (Frank J. Seiler Research Lab., USAFA) [8-10]. Viscosity and conductance data are available but the optical properties of these molten salt systems have not been investigated so far.

Aluminum chloride and 1-butylpyridinium chloride, and other chemical syntheses, are presently being performed in the laboratory of Dr. R. Job, Chemistry Department, CSU. Materials are then transferred to a Vacuum Atmospheres drybox facility which has been assembled at the Electrical Engineering Department, C.S.U. This inert atmosphere module is being utilized for the cell and electrolyte testing of air sensitive (oxygen and/or moisture) PECs. Aqueous electrolytes are being prepared by conventional procedures. Kohl and Bard [11] have recently demonstrated that trace amounts of water in acetonitril electrolytes can markedly affect the performance of n-GaAs electrodes.

In order for an electrolyte to be suitable for a particular PEC application, it is important that it contain an appropriate redox system. The concentrations of the reductant and oxidant components must be such that the electron (hole) transfer processes at the semiconductor and

counter electrodes of the cell can sustain "Tafel" currents at the maximum cell operating efficiency. Accordingly, it is important that both redox components are sufficiently soluble in the electrolyte solvent, as well as having adequate long-term chemical stability. In general, there has been relatively little fundamental work on the redox properties of inorganic or organic couples in the AlCl_3 :1-BPC room temperature melt (although more extensive data exists for the high temperature chloroaluminate systems e.g. [12]). We plan to survey a number of likely candidates that may meet the operational requirements of solubility and appropriate standard potential. Measurements of the solubility of ferrocene in the 1:1 AlCl_3 :1-BPC melt at $30 \pm 1^\circ\text{C}$ indicate a high solubility ($\sim 0.45\mu$) and a sample of ferricenium chloride has been prepared by Dr. Job and will shortly be the subject of solubility measurements and electrochemical stability investigations. Together with the appropriate Tafel characteristics at the counter electrode, it should prove possible to define the operational and geometrical requirements for a prototype cell of the type n-GaAs//Ferrocene/ferricenium chloride/ AlCl_3 : 1-BPC//C.

Finally, it should be emphasized perhaps that chloride ion based ambient temperature molten salt may not be the best choice from liquidus range or semiconductor electrode corrosion. A survey of alternative ambient temperature molten salts will be made.

II.1.2 Novel Approaches

An alternative, very promising approach to achieve high concentrations of the liquid phase redox carrier couple might be to prepare electrolytes whose integral components comprise the redox couple. For example, the

FeII/FeIII couple may be a suitable redox couple for n-GaAs and we have found that a FeCl_3 :1-BPC mixture is liquid at ambient temperatures. The ternary system $\text{FeCl}_2/\text{FeCl}_3$ /1-BPC can be characterized when a sample of FeCl_2 is available. This approach would enable extremely high concentrations of the primary redox components and thereby permit the maximum electron transfer efficiencies as well as to assist to minimize the competitive corrosion reactions (photo-dissolution) of the semiconductor electrode effectively. We are intending also to assess the alkyl-substituted ferrocene/ferricenium halides, both for redox behavior and as possible candidates for melt components of possible ambient temperature systems.

II.2 Fabrication and Evaluation of Electrodes

II.2.1 Transition Metal Sulfides and Disulfides

Dr. Job has obtained a multiple zone furnace (Marshall Furnace model no. 1037) and a controller is being constructed. Syntheses have been selected for preparing precursors for thin film materials of Mo compounds. A natural sample of MoS_2 (molybdenite) was obtained but some preliminary Hall measurements indicated that this material was unsatisfactory for semiconductor use.

II.2.2 Ternary Chalopyrite Electrodes

Some electrochemical experiments have been initiated with a commercial sample of CuInSe_2 in aqueous pH buffers of 2, 4.8, 9.2 and 12. Cyclic voltammetry has indicated that small faradaic currents are found over most of the potential window, whose stability is approximately +0.5 to -0.6 V SCE. No large photo-corrosion was detected, however, and additional experiments are planned with redox additions. Capacitance/voltage curves exhibited considerable hysteresis, presumably because of

the faradaic impedances throughout the potential window and estimations of the flat-band potential may be difficult for these materials.

II.2.3 GaAs, Si etc.

Tin-doped n-GaAs semiconducting electrodes have demonstrated large photoeffects in 1:1 molar ratio AlCl_3 :1-BPC electrolyte and we are currently engaged in additional optimization studies prior to prototype cell construction, based on the ferrocene/ferricenium chloride redox couple. Normal pulse polarography is being used to estimate optical efficiencies, which appear to be reasonably high (>6%). These studies should aid delineation of the experimental data required for evaluation and construction of practical cells. A flow-chart (Table I) highlights the data acquisition and feedback interaction parameters involved to achieve an operational cell design. A large photo-dissolution effect has been detected for n-GaAs in the absence of a redox couple (vide infra II.3). The n-GaAs flat-band dependence [1,2] on the melt pCl^- suggests that surface equilibria processes are significant. The role of such surface modifications vis a' vis the rates of electron transfer and as recombination centers is poorly understood. Two methods may be applied to study and hopefully gain some understanding of the significance of these effects (i) impedance equivalent circuit modelling by network analysis or quantitative correlation of band edge shifts with electrolyte composition variations (pCl^-), and (ii) surface analyses by Auger/ESCA, to define the chemical surface constitution.

Preliminary electrochemical experiments with a single crystal silicon electrode in the 2:1 AlCl_3 : 1-BPC melt have shown that surface faradaic reactions occur throughout the stability window of the solvent. These may arise from surface modification (chlorination of terminal crystal

atoms) or because of incomplete removal of oxide layers. Again, Auger/ESCA techniques may be valuable experimental aids to study the semiconductor surface but further surface preparation studies are needed before any final conclusions regarding photoeffects on Si can be made. Tyagai and coworkers [13] recently have studied single crystal silicon electrode behavior in the high temperature chloroaluminate melts. Values of the steady-state potential of Si were found to depend markedly on the composition of the gas phase in contact with the melt (air, Cl_2 or argon). Current yields for the anodic oxidation of Si were close to 100% and the chief product thought to be SiCl_4 . Further studies of the Si electrode in room temperature melts are being planned.

II.3 Photo-Corrosion Studies

Gerischer has asserted [14] that "the greatest obstacle to the utilization of photoelectrochemical cells is the susceptibility of the semiconductor electrode to corrosion" and "all semiconductors seem to be thermodynamically susceptible to anodic photo-decomposition in aqueous solutions." If these statements are essentially true, the rationale for choosing non-aqueous systems for investigation is justified and it then becomes necessary to obtain some estimate or guidelines for the thermodynamical stability of semiconductor electrodes in non-aqueous electrolytes. We have performed preliminary electrochemical measurements (cyclic voltammetry and normal pulse polarography) on the photo-corrosion of n-GaAs in the 1:1 molar ratio AlCl_3 :1-BPC melt. Equipment has been ordered to perform rotating ring-disc electrode measurements which hopefully will enable us to identify corrosion products more definitively. Unfortunately, there have been few reliable studies of arsenic compounds in chloroaluminate melts,

although the electrochemistry of gallium has been characterized fairly well [15]. Our experiments on the electrochemistry of GaCl_3 and AsCl_3 added to a 1:1 melt, suggest that the corrosion process may be represented by the equation:

with the formal oxidation state of arsenic changing from -3 to +3. In a basic (Cl^- - rich) melt these tri-chlorides possibly will form complex ions, but again there is little fundamental knowledge for these systems. Calculations are being made (to be reported later) to determine the theoretical free energy balance for probable corrosion mechanisms and to aid understanding of the factors affecting the corrosion processes in non-aqueous molten salt liquids. Table II lists the melting points of a series of chloride complexes. If a rough correlation exists between the melting point and solubility of a particular compound, this would suggest that AsCl_3 and GaCl_3 may be particularly prone to dissolve in the room temperature melts. On the other hand, semiconductors such as CdS , CdSe and CdTe may not be soluble and this factor could help to lower photo-corrosion. Obviously, too the reduction/oxidation behavior will be critically important. Examination and comparison of a series of such semiconductor electrodes may help to predict the important factors of corrosion. Table III lists some of the known redox potentials for simple inorganic compounds in low-temperature chloroaluminate melts.

III. SUMMARY OF PROGRESS

It has been demonstrated for the first time that a semiconductor electrode exhibits quite large photoeffects in a cell containing a molten salt electrolyte. Detailed studies are underway to explore the constraints and advantages of this type of electrolyte, from the standpoint of efficiency, corrosion of the electrode, and the chemical and physical properties related to overall cell performance. We feel that the multidisciplinary approach to the conceptual problem of practical cell construction is an important ingredient for the ultimate success of this type of program and that considerable effort will be needed to properly evaluate the potential of non-aqueous electrolytes in PEC cells.

IV. STATUS OF DELIVERABLES

- Objective I
- A. Achieved and in hand
 - B. Equipment being prepared
 - C. Contingent on A and B above

Objective II

So far, n-Si has been studied by cyclic voltammetry in the 2:1 AlCl_3 :1-BUPyCl melt. No large photo-effects could be detected and the condition of the surface seems to be a prime importance.

Objective III

Two papers have been written to date on the performance of the n-GaAs electrode in the AlCl_3 :1-BuPyCl room temperature electrolyte. Experiments are in hand to optimize a prototype cell.

Objective IV

Fabrication procedures for n-MoSe₂ electrode underway

Objective V

A single crystal CuInSe₂ electrode has been studied in 4 aqueous pH buffers and further attempts are underway to understand its electrochemical behavior.

Objective VI, VII and VIII

These objectives are to be commenced at a later date when experimental cell performances are better evaluated.

V. TABLE I

V. TABLE II

Melting Points of Chlorides ($^{\circ}\text{C}$)

Al Cl_3	190	{ Ga Cl_2	164	Pb Cl_2	501
As Cl_3	-8.5	{ Ga Cl_3	78		
Ag Cl	455	Ge Cl_4	-49.5	Ru Cl_3	d>500
		{ Hg ₂ Cl_2	400 subl.	Si Cl_4	-70
{ Bi Cl_3	230-32	{ Hg Cl_2	276	{ Tl Cl	430
{ Bi Cl_4	226			{ Tl Cl_3	25
		{ In Cl_2	235	{ Ti Cl_2	d475
Cd Cl_2	568	{ In Cl	225	{ Ti Cl_3	660
Ce Cl_3	848	{ In Cl_3	300 subl.	{ Ti Cl_4	136
{ Co Cl_2	724				
{ Co Cl_3	subl.	{ Mn Cl_2	650	{ U Cl_3	842
Cu Cl	430	{ Mn Cl_3	decomp.	{ U Cl_4	590
Cu Cl_2	620	{ Mo Cl_3	d		
		{ Mo Cl_4	d	{ W Cl_2	-
{ Eu Cl_2	727	{ Mo Cl_5	194	{ W Cl_4	d
{ Eu Cl_3	850			{ W Cl_5	248
		Mg Cl_2	708	{ W Cl_6	275
{ Fe Cl_2	670	{ OS Cl_2		Zn Cl_2	283
{ Fe Cl_3	305	{ OS Cl_3	500d	{ Zr Cl_2	d350
		{ OS Cl_4	subl.	{ Zr Cl_3	d350
				{ Zr Cl_4	437

V. TABLE III

<u>Couple</u>	<u>E° molar/V</u>	<u>Ref.</u>
Ga(I)/Ga(0)	0.199	14*
Ga(III)/Ga(0)	0.577	"
Ga(III)/Ga(I)	0.766	"
ln(III)/ln(I)	1.1	"
Zn(II)/Zn(0)	0.254	"
Cu(II)/Cu(I)	1.851	9**
Cu(I)/Cu(0)	0.777	"
Fe(III)/Fe(II)	2.012 (2:1 solvent)	10***
Fe(III)/Fe(II)	0.125 (1:1 solvent)	10****

* Potentials versus Al/Al³⁺ in AlCl₃/NaCl/KCl eutectic, 135°

** Potentials versus Al/Al³⁺ in 2:1 AlCl₃:1-MePyCl, 30°

*** Potential versus Al/Al³⁺ in 2:1 AlCl₃:1-BuPyCl, 30°

**** Potential versus Al/Al³⁺ in 2:1 AlCl₃:1-BuPyCl, 35°

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