

it clearly demonstrates that the a-B:H film, in spite of its low carrier mobility (usually signaled by high resistivity), still exhibits a photoelectrochemical effect. It is then reasonable to expect that such an effect can be enhanced through the improvement of the semiconducting properties of thin n-type Si-doped a-B:H thin films.

It has been established that the chemical stability of the a-B:H film produced by the glow discharge of diborane is stable in both aprotic and alcoholic solvents. It is also more resistant to dissolution in aqueous electrolytes than would be expected based solely on thermodynamic considerations.

In conclusion, it was found that the highly resistive n-type Si-doped a-B:H prepared in this work indeed exhibits a small photoelectrochemical effect. Its semiconducting properties must be further modified to favor a more enhanced photovoltage to be considered as a suitable electrode material for a photoelectrochemical cell.

MOLTEN SALT CELL RESEARCH

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The objective of this project is to conduct the research required to develop cells for an advanced electric-vehicle battery that has very high specific energy and power, long cycle life, and an acceptable cost. The performance and lifetime goals for the cells are a minimum specific energy of 160 W h/kg (3 h discharge rate), volumetric energy density of 400 W h/l, peak specific power of 240 W/kg (20-s pulse at 50 percent discharge), and lifetime of 1000 cycles. Although the present emphasis is on lithium-alloy (e.g., Li-Al, Li-Si, Li-Al-Si) negative electrodes and transition metal disulfide (FeS_2 and NiS_2) positive electrodes, other active materials are also under consideration.

During 1982, this project consisted of four tasks: negative electrode research, positive electrode research, materials research, and electrode and cell modeling. The major accomplishments during this period were as follows:

- A determination of the sequences of phases formed during the discharge of FeS_2 , NiS_2 , and CoS_2 electrodes was completed.
- The electromotive force (emf) for the first discharge reaction of the FeS_2 electrode ($\text{FeS} + \text{Li}_3\text{Fe}_2\text{S}_4$) has been determined as a function of temperature; preliminary emf data have been obtained on the discharge of NiS_2 to NiS.

- The solubilities of Li_2S in LiCl-KCl (at 49.1, 58.2, and 69.6 mol% LiCl) and in LiF-LiCl-LiBr (22-31-44 mol%) have been determined as a function of temperature.
- The $\text{Ni/Ni}_3\text{S}_2$ electrode was shown to exhibit a Nernstian response to sulfide ion concentration in LiCl-KCl electrolyte, and an analytical method for metal sulfides in molten salt electrolytes was developed on the basis of these data.
- *In situ* spectroscopic studies were conducted on polysulfide species in molten LiCl-KCl . There appears to be a linear correlation between the frequency of the absorption peak and the reciprocal of the value of x in S_x^{2-} .
- Morphological studies of Li-Si and Li-Al-Si electrodes have shown a porous microstructure with some similarity to Li-Al microstructure; the Li-Al-Si showed a duplex structure of porous Li-Al and nodules of LiAlSi .
- Area specific resistance (ohm cm^2) values of a lithium-silicon electrode were determined over the composition range of $\text{Li}_{3.17}\text{Si}$ to $\text{Li}_{0.95}\text{Si}$. The area-specific resistance values increased with the number of cycles the electrode had undergone.
- Power measurements on a lithium-silicon electrode showed a significant decrease in the power as the electrode was discharged from $\text{Li}_{2.85}\text{Si}$ to $\text{Li}_{1.68}\text{Si}$.
- Diffusion couple measurements were made to determine the rate of aluminum attack on iron in negative electrode current collectors.
- A potentiostatic technique was used to evaluate the integrity of coating materials (e.g., Ni , TiN , TiC) on low-carbon steel.
- Studies of ceramic powder (e.g., MgO) separators have shown that the use of a very fine powder results in inadequate strength of the separator, whereas the use of a coarse powder does not provide adequate particle-retention characteristics. It appears that optimum separator properties will result from the use of a combination of particle sizes.
- A computer program that was developed to predict the performance of full-scale Li-Al/FeS cells of various designs from small-scale cell results and basic electrochemical information has been extended to accommodate cells having other active materials and electrolyte compositions.
- To provide input data for the above program, four small-scale (25 to 35 A h theoretical capacity) Li-Al/FeS_2 cells were built and placed on test. After 44 to 80 cycles, all four cells show no measurable capacity decline or energy loss.

The work planned for 1983 is aimed primarily toward lithium alloy/molten salt/transition metal disulfide cells, and the major activities are as follows.

Electrochemical research

-The solubilities of the electrode materials in molten-salt electrolytes at various states of charge will be determined.

-Thermodynamic data will be acquired through potentiometric titrations of each electrode material.

-The kinetic characteristics of the electrode materials in selected electrolytes will be evaluated by a combination of galvanostatic cycling, d.c. relaxation measurements, pulse measurements, and cyclic voltammetry.

Materials Science

-The corrosion of ceramics, alloys, and coated materials will be investigated by static immersion tests, potentiostatic-galvanostatic tests, and post-test examinations of components from small cells.

-Composition profiles within the electrodes of experimental cells will be determined.

-Equilibrium composition data (*i.e.*, phase diagrams) will be developed on electrode materials with emphasis on certain ternary alloys based on the Li-Si and Li-Al systems.

-The effects of particle size, shape, and area on the physical properties of powder separators will be evaluated.

Electrochemical engineering

-Parametric studies of cell energy, power, and lifetime will be conducted in small (30 to 50 A h) experimental cells to determine the effects of operating conditions and cell design variables.

-The computer program developed in 1982 will use the above data to estimate the performance of full-scale cells of various designs.

Recent publications

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THERMAL MANAGEMENT OF BATTERY SYSTEMS

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The objectives of this project are to determine heat generation rates, measure temperature distributions, analyze heat transfer rates, and evaluate thermal management strategies for Li/MS batteries.

- A high-temperature calorimeter was built for measuring cell heat generation. The operating ranges of temperature and heat flow are room temperature to 500 °C and 0 to 50 W, and the detection limit is 1 mW.
- A constant-temperature furnace was built for precise cell electromotive force (emf) and overpotential measurements. The temperature distribution in the test chamber varies less than 1 °C at temperatures up to 500 °C.
- The temperature distribution in a 2.5-kW h LiAl/FeS battery was measured under a variety of operating conditions.
- A forced-air cooling system was designed and tested; it provided 1.0 to 1.5 kW of cooling to a 2.5-kW h battery at an air flow of 750 scfh.
- Cell reversal adversely affected battery performance, as expected, but also created hot spots during operation.
- The temperature coefficient of emf of LiAl/FeS cells was measured. It is a complicated function of temperature, state of charge, and electrolyte composition.
- The rate of thermal energy generation was calculated from a thermodynamic equation. The results were in good agreement with the heat flow measured with the high-temperature calorimeter.