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MATERIALS CHALLENGES IN ELECTROCHEMICAL ENERGY STORAGE SYSTEMS

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Abstract - A rechargeable electrochemical cell with an alkali-metal electrode is a very efficient method of high energy storage. The electrochemical principles and materials properties necessary to achieve high energy density and extended lifetimes in new rechargeable electrochemical cells are summarized. The important cell materials are electrodes, electrolytes and containers. Major materials challenges exist in the development of improved high-energy cathode materials, of chemically-stable, fast-ion solid electrolytes and of all solid-state lithium cell. Currently, the most attractive electrode and electrolyte materials (i.e., TiS_2 and sodium beta" alumina) have a two-dimensional layer structure and exhibit a unique combination of rapid transport properties and high chemical stability. Amorphous disulfide cathodes, divalent beta"-alumina electrolytes and sodium-ion glass electrolytes have particularly attractive applications in future energy-storage systems.

INTRODUCTION

Electrochemical energy-storage systems or batteries have many advantages and applications. The most attractive new rechargeable batteries are those which use alkali-metal electrodes, particularly lithium and sodium, because of their intrinsically high-energy storage capabilities. The development of new high-energy, rechargeable batteries is hampered by a number of materials problems, and the current status of the material challenges in alkali-metal electrochemical cells is discussed in this paper. After describing some general electrochemical principles and the desirable materials properties of electrochemical-cell components, the materials challenges are summarized in three types of cells: Solid Electrode-Liquid Electrolyte Cells, All Solid State Lithium Cells and Liquid Electrode-Solid Electrolyte Cells.

Several general principles of electrochemical cells can be summarized using equations (1) and (2), where V is the cell voltage, μ_A' and μ_A'' are the chemical potentials of the alkali metal in electrodes ' and ", respectively, F is the Faraday constant, n is the charge of the alkali-metal, i is the cell current, R is the cell resistance and η is the cell overvoltage (1).

$$V = 1/nF(\mu_A' - \mu_A'') \quad (1)$$

$$V = i\,R + \eta \quad (2)$$

Equation (1) illustrates that the cell voltage or energy density is established by the chemical-potential difference between the two electrodes. Because extremely large chemical-potential differences are possible with alkali-metal electrodes, these systems are the most attractive candidates for new high-energy rechargeable batteries. Equation (2) indicates that, for a given cell voltage established by Eq. (1), the cell current is maximum when the cell resistance and overvoltage are minimized. Indeed, the two materials research approaches directed toward the development of new rechargeable electrochemical cells are fast-ion conducting electrolytes which would minimize R and novel electrode materials with minimal overvoltage characteristics (1).

In rechargeable electrochemical cells, the liquid-solid interface has distinct advantages over a solid-solid interface in minimizing charge-transfer overvoltages and in adjusting to the volumetric changes which occur in the electrodes during current flow. Thus most of the research with rechargeable cells has emphasized either solid electrode-liquid electrolyte cells or liquid electrode-solid electrolyte cells. However, there are several recent research programs designed toward the development of all solid-state rechargeable lithium cells.

The desirable properties of the electrolyte, electrodes and container materials for rechargeable alkali-metal cells are summarized in Table 1. A useful electrolyte must have negligible electronic conductivity and the necessary chemical stability, in addition to being a fast-ion conductor. The electrodes must not only have the necessary chemical potential values as illustrated in Eq. (1), but also must exhibit rapid alkali-metal diffusion or transport to minimize the overvoltage, η, in Eq. (2). Electrodes with good electronic conductivity eliminate or minimize the need for a current conductor, which is used, for example, in the PbO_2 electrode in the lead-acid cell. If the cell container is a good electronic conductor, it can also provide electrical contact to one electrode. However, any acceptable container material must have the necessary chemical stability to minimize or avoid chemical reactions with the electrodes and/or electrolyte. Such corrosion reactions can be particularly significant with liquid cell components at elevated temperatures.

TABLE 1. Desirable properties of materials in rechargeable alkali-metal cells

Cell Materials	Desirable Properties
Electrolyte	- Fast Ion Conductors - Negligible Electronic Conductivity - Chemical Stability
Electrodes	- Proper Values of μ_A - High Transport of A - Good Electronic Conductor
Container	- Chemical Stability - Good Electronic Conductor

SOLID ELECTRODE-LIQUID ELECTROLYTE CELLS

The recent successful developments of high-energy primary lithium batteries at ambient temperatures have stimulated increased research and development of rechargeable lithium cells using organic solvent electrolytes. If the lithium cell represented in cell (A) is a primary cell, the cathode accepts lithium ions during a single discharge. However, the cathode material of a rechargeable cell must be capable of reversibly accepting and rejecting lithium ions during many cycles.

Li/organic solvent with Li^+/cathode (A)

A major materials challenge in ambient-temperature, rechargeable lithium cells is the selection of an optimum cathode material which maintains its reversibility and high capacity for lithium after extended cell cycling. A second challenge is the control or avoidance of a lithium anode film which causes cell failure and low cycle life.

Cathode Materials

The cathode material in cell (A) must be able to rapidly accept and reject lithium ions during cell cycling to minimize polarization losses (illustrated by the η term Eq. 2) due to concentration gradients in the electrode. The Group IVB, VB and VIB transition-metal disulfides have a rather unusual two-dimensional layer structure which can intercalate lithium rapidly and reversibly (2,3) as illustrated schematically in Fig. 1.

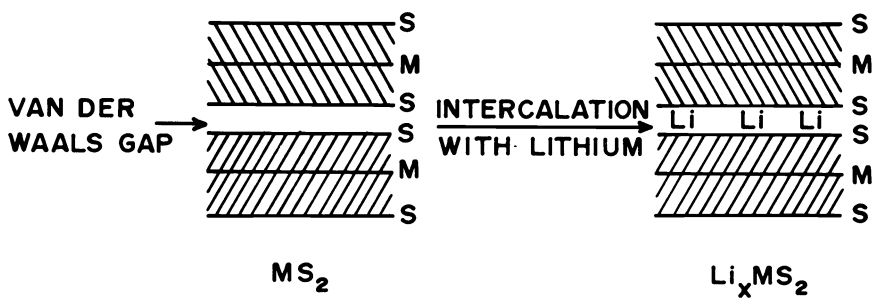

Fig. 1. Schematic illustration of lithium intercalation into the van der Waal's gap between the sulfur layers.

Although the observed high lithium diffusivities (3) in the two-dimensional van der Waal's gaps shown in Fig. 1 are not surprising, such rapid transport is usually incompatible with the strong chemical bonding and the low lithium chemical potential required for a high-energy cell. However, some intercalated disulfides have a unique combination of high diffusivities and low chemical potentials of the alkali-metal intercalants (2). The low chemical potentials are due to the phase relationships which exist in the ternary alkali metal-transition metal-sulfur systems. For example, the isothermal ternary section for the Li-Ti-S system is shown in Fig. 2.

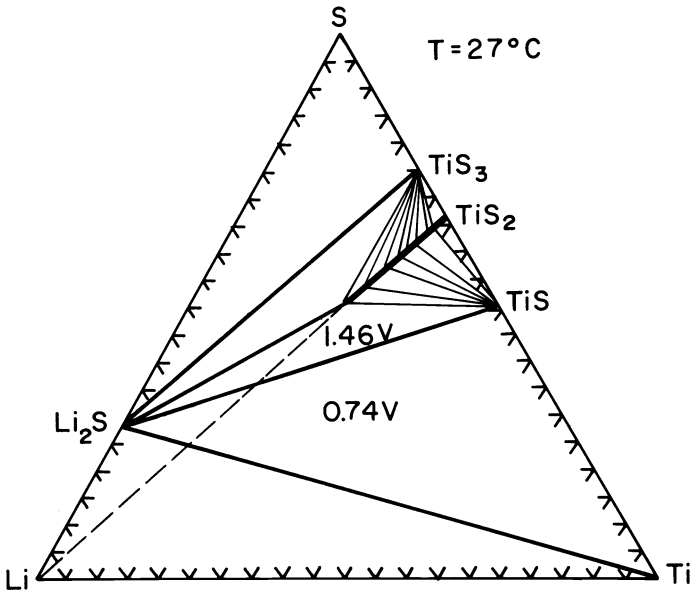

Fig. 2. Isothermal section for the Li-Ti-S ternary system at 27°C. The equilibrium cell voltage for three-phase cathode mixtures versus a lithium anode are illustrated in two of the three-phase regions.

The intercalated $LiTiS_2$ phase is illustrated by the thick solid line extending from TiS_2 toward the lithium corner in Fig. 2. When a Li/TiS_2 cell is discharged, lithium is removed from the lithium anode and is intercalated into the TiS_2 cathode. If the cell is discharged beyond the capacity of the TiS_2 to intercalate lithium, the dotted line in Fig. 2 indicates that the $LiTiS_2$ electrode would react with the excess lithium to form Li_2S and TiS. Because the lithium chemical potential remains low in the three-phase ($LiTiS_2$ - Li_2S) region, the equilibrium cell voltage remains relatively high at 1.46 volts. If the cell is discharged below 1.46 volts, the $LiTiS_2$ phase disappears and titanium metal is formed. As shown in Fig. 2, the calculated equilibrium cell potential for the three-phase (Li_2S - TiS - Ti) cathode region is 0.74 volt.

Although numerous transition-metal disulfides can intercalate lithium, TiS_2 is the most popular disulfide cathode because it has the highest energy density (2,4). Two of the most attractive alternatives to TiS_2 for ambient-temperature, rechargeable lithium batteries are V_6O_{13} (5) and amorphous MoS_2 (6). The V_6O_{13} compound has a perovskite-type structure which contains an extended network of cuboctahedron cavities in which lithium ions are mobile (5). The cell performances of V_6O_{13} and TiS_2 are very comparable. However, highly lithiated V_6O_{13} is a poor electronic conductor, and additional material, such as carbon, must be in the cathode to maintain cell capacity.

Amorphous disulfides also merit further investigation as cathode materials. Initial results with amorphous MoS_2 (4,6) indicate that high cell capacity is maintained even after extended cycling. However, the energy density of MoS_2 is not significantly better than that of TiS_2, and the low electronic conductivity of lithiated MoS_2 could also be a problem.

Lithium Anode Film

A major challenge in the successful development of rechargeable, ambient-temperature lithium cells with extended cycle lives is the control or avoidance of the lithium anode film. Such film formation can isolate areas on the anode from lithium deposition. In other anode regions of preferential lithium deposition, dendritic type lithium columns grow into the electrolyte, resulting in the eventual contact with the cathode and cell failure. The

longest reported cycle life is 260 cycles for a Li/V_6O_{13} cell with a $LiAsF_6$ salt dissolved in 2 Me (methyl acetate) - THF (tetrahydrofuron) solution (7).

In a recent review of the recharging problems of the lithium electrode (4), it is not clear whether film formation is due to electrolyte impurities or to the fundamental thermodynamic instability of lithium in organic solvent electrolytes. However, results using advance surface-spectroscopy techniques to examine lithium anode films, indicate that lithium reacts with both the $LiAsF_6$ salt and the 2 Me - THF solution (8). These results and others (4) strongly suggest that lithium anodes are chemically reactive in all organic-based electrolytes. Thus the nature, morphology, structure and properties of the anode film are major factors in cell performance and cycle life. A major research challenge is the development of methods or unique liquid electrolytes to form a uniform film with the necessary conduction properties to enable the reversible removal and addition of lithium over extended cell cycles.

Elevated-Temperature Lithium Cells

There has been extensive research and development of Li/FeS cells using a LiCl-based molten salt at 400-500°C (9). The major technical challenges are the development of a leak-tight feedthrough and an economically attractive separator material. A leak-tight feedthrough would enable the cells to attain increased lifetimes in air environments. Expensive BN felt has been used to separate the lithium from the FeS electrode. However, MgO separators are being developed to replace the BN felt (9). Because an acceptable separator must be chemically inert in the LiCl-based liquid electrolyte, the number of candidate materials is extremely limited.

ALL SOLID-STATE LITHIUM CELLS

An all solid-state lithium cell would avoid the previously discussed lithium anode film problem. However, the preservation of structural integrity at the electrode-electrolyte interface is a major challenge because of the volumetric changes in the electrodes which occur during cycling. Three types of solid-state cells are being actively investigated.

The first type, which is being developed by Hitachi, in Japan, is a thin-film Li/TiS_2 cell using a 2-4 μm thick amorphous $Li_{3.6}Si_{0.6}B_{0.4}O_4$ film as the electrolyte (10). The lithium-ion conducting film has a relatively low resistivity (~10^5 ohm-cm) at 25°C, good thermal stability and good stability with respect to the electrode materials. Surprisingly, only minor breakdowns at the electrolyte-TiS_2 interface due to the 10% c-lattice expansion of TiS_2 have been observed (10). The thin-film cell has been discharged about 2000 times. Although the cell currents are rather low (6-16 $\mu A/cm^2$), the cell could be a feasible small power source for low-current electronic devices.

The second type of solid-state lithium cell uses a polymer electrolyte, which should have the plasticity to absorb volumetric charges in the electrodes during cycling. The most popular cathode material for the polymeric electrolyte cells are TiS_2 and V_6O_{13}. Complexes formed between polyethylene oxide (PEO) and salts having large anions are the most studied polymeric electrolytes (11). It is now known that ionic conduction occurs in the amorphous domains rather than in the crystalline phases of these polymeric complexes. The resistivity of polymeric electrolytes such as the PEO-$LiCF_3SO_3$ and PEO-$LiClO_4$ complexes is 10^4 at temperatures between 50 and 120°C (11). Although there is general agreement that the electronic conductivity is negligible, the magnitude of the anionic contribution is a controversial issue with reported values ranging from 10 to 90% depending upon the measurement technique (11). Thus accurate values for the anionic contribution to the conductivity must be obtained, and the effects of the anionic contribution upon electrode-electrolyte interfacial reactions, polarization and cell performance must be evaluated. There are numerous laboratories investigating the performance and cycle life of polymeric cells, and many results should be published in the near future.

The third type of solid-state lithium cell has a two-phase or composite lithium electrolyte. In 1973 it was reported that the addition of Al_2O_3 to a LiI electrolyte increased the ionic conductivity by two to three orders of magnitude (12). Recently several investigators have confirmed that the conductivity enhancement is due to the rapid ionic transport along the numerous LiI-Al_2O_3 interfaces in the composite electrolyte (12-15). An obvious but exciting research challenge is the similar conductivity enhancement of other solid electrolytes by the addition of chemically inert compounds.

LIQUID ELECTRODES-SOLID ELECTROLYTE CELLS

The advantages of solid-electrolyte cells are: the elimination of a separation material, negligible self discharge on storage and possible application of the thin-film fabrication techniques used in the semiconductor field. The most popular solid-electrolyte cell is the

sodium-sulfur (Na/S) system which is considered by many to be the best candidate for a new high-energy rechargeable battery (9). The Na/S cell, which operates at 300-400°C, consists of a liquid sodium anode and a liquid sulfur electrode separated by a beta"-alumina electrolyte tube. Both sodium and beta" alumina crystallize in a layer structure. Rapid sodium ion conduction occurs in the two-dimensional planes, which are bounded by two close-packed layers of oxygen atoms held apart by Al-O-Al columns (16). Because the sodium-ion conductivity in beta" alumina is four to six times that in beta alumina, the former is the preferred electrolyte. The Na/S cell has no self-discharge on storage, can be thermally cycled, and is a completely sealed system. Two major materials challenges are the reduction of premature failures of the beta" alumina tubes and the development of a low-cost, corrosion-resistant container for the liquid sulfur electrode.

Although lifetimes of over 1,200 cycles have been achieved, a number of Na/S cells have failed prematurely due to asymmetric polarization and dendritic penetration of sodium into the beta" alumina electrolyte at the sodium-electrolyte interface (9). Recently the sodium ejection and uptake at a beta"-alumina surface at temperatures between 100 and 400°C have been directly observed using a hot stage in a scanning electron microscope (17). The beta" alumina surface is poorly wetted by liquid sodium when the temperature is less than 300°C. Other observations indicate that the individual grains or crystals at the polycrystalline beta"-alumina surface are properly oriented for uniform sodium-ion conduction (17). However, the observed formation of sodium oxide on part of the electrolyte surface could lead to selective regions of current intensification and eventual fracture of the electrolyte.

Another materials challenge in the Na/S cell is the corrosive nature of the sulfur electrode, particularly the polysulfide melts. The container material for the sulfur electrode must form a protective sulfide layer with good electronic conductivity, because the container also serves as the cathode current collector. The most protective sulfide layers are Cr_2S_3, Al_2S_3 and MoS_2; thus a number of economically acceptable alloys or coatings which could form these sulfides in the sulfur-electrode environment are being investigated (18).

In addition to the sodium beta"-alumina cell, two other recent solid-electrolyte developments merit particular attention. The first is the discovery that divalent cations can be completely substituted for sodium in beta"-alumina (19). As shown in Fig. 3, the divalent beta" aluminas are good ionic conductors. At 40°C the conductivitiy of lead beta" alumina is about 1000 times greater than that of the other divalent beta"-aluminas and only slightly less than that of sodium beta"-alumina. The conductivity results shown in Fig. 3 are for single crystals, and the fabrication of high-density polycrystalline forms with acceptable mechanical strength is a major materials challenge.

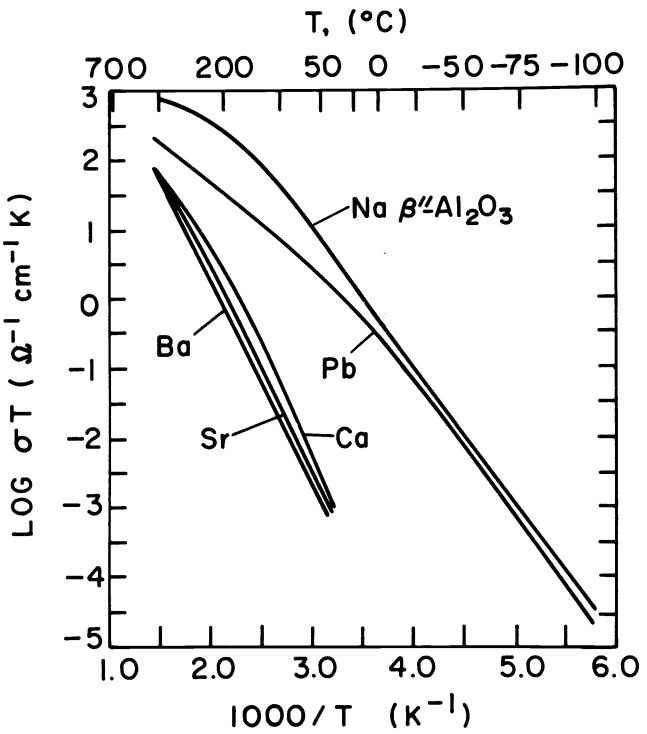

Fig. 3. Comparison of the ionic conductivities of Pb, Ca, Sr and Ba divalent beta" aluminas with that of sodium beta" alumina (19).

The second attractive solid-electrolyte is an ion-conducting glass with good conductivity and chemical stability. Because the known lithium-conducting glasses have low chemical stabilities leading to decomposition problems in electrochemical cells, the sodium-ion glasses have the best potential in cell applications. The advantages of sodium-ion glasses over other ceramic electrolytes include their low cost, ease of fabrication, high strength in thin sections and the absence of grain boundaries. The two major research challenges are decreasing the resistivity and increasing the chemical stability. New sodium-conducting glasses have been reported (20) with resistivities as low as 10^3 ohm-cm, which is significantly lower than the 10^5 ohm-cm value of the doped borate glass used in a hollow-glass fiber Na/S cell (21). However, the chemical stability of these new glass electrolytes (20) must still be improved to insure their stability in a Na/S cell.

SUMMARY

The most useful electrode and electrolyte materials are those having a two-dimensional layer structure, particularly the TiS_2 electrodes and the beta" alumina electrolytes. These materials have a unique combination of rapid transport properties and high chemical stabilities in electrochemical cells.

Some of the materials challenges in the development of new rechargeable alkali-metal cells have been discussed. In ambient-temperature lithium cells, cell capacities and cycle lives must be increased by new developments in cathode materials and improvements in the lithium anode films. New solid-state rechargeable lithium cells can be anticipated with the discoveries of new composite electrolytes and polymeric electrolytes with negligible anionic conductivity. Advances in our understanding of the interfacial reactions at the sodium electrode-beta" alumina interface and at the sulfur electrode-container interface should lead to increased reliability and cycle life of the Na/S cells. The successful fabrication of polycrystalline divalent beta" aluminas and chemically stable sodium-conducting glasses would stimulate the development of new solid-electrolyte cells.

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