Sodium/Phosphorus-Sulfur Cells

I. Cell Performance

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ABSTRACT

Sodium/β''-alumina/phosphorus-sulfur cells utilizing P/S ratios of 0, 0.143, 0.332, and 1.17 at temperatures from 350 to 500°C were studied by measurement of the equilibrium cell voltages at open circuit, and the steady-state cell voltages at current densities up to 70 mA/cm². States of charge, represented by sodium atom fraction in the P-S electrode, ranged from 0 to 0.4. Open-circuit voltages up to 2.65 V were measured. Theoretical specific energies up to 825 Wh/kg were calculated from the open-circuit potential *vs.* composition data. When phosphorus was added to the sulfur electrode in the P/S ratio 0.143, the cell resistance was two to ten times greater than that with sulfur alone.

Introduction

The sodium/sulfur (Na/S) cell has been the subject of research and development for nearly thirty years.[1] Factors which determine the performance of the sulfur electrode include conductivity as influenced by viscosity and ionic strength, the energy of the reaction with sodium, the number of liquid phases (one or two) present, and the effective equivalent weight of the sodium-sulfur combination.

The characteristics of the sulfur electrode, the properties of phosphorus sulfides, and the results of previous work with lithium/phosphorus-sulfur cells indicate that sulfur electrode performance in the Na/S cell might be improved by the addition of phosphorus.[2] The purpose of this work was to evaluate phosphorus as an additive to the sulfur electrode in Na/S cells.

Equilibrium open-circuit voltage (OCV) measurements.—A first step in the evaluation of sodium/phosphorus-sulfur (Na/P-S) cells is the measurement of the equilibrium OCV at various states of charge, temperatures, and P/S ratios. The information thereby obtained is thermodynamic rather than kinetic and has the advantage of being independent of cell geometry. Equilibrium OCV measurements were used as a screening method to determine temperatures and phosphorus-sulfur mixture compositions which may give higher performance than that of the pure sulfur electrode.

Integration of a plot of equilibrium cell voltage *vs.* charged passed gives the theoretical maximum energy which could be obtained from a cell if it is discharged "reversibly" (infinitely slowly). The theoretical maximum specific energy (Sp.E.) available from the discharge of a cell can be calculated as follows

$$Sp.E. = \frac{\int_0^\alpha \epsilon(c)dc}{m_{Na} + m_{PS}}$$

where α is the number of coulombs of charge c required to discharge a fully charged cell to a cell potential that determines the end of discharge (usually 1.6 V); m_{Na} is the mass of the sodium involved in the passage of α coulombs; m_{ps} is the mass of all of the phosphorus and sulfur in the positive electrode; and $\epsilon(c)$ is the cell OCV. The integral was evaluated graphically. The result of this calculation from our sodium/sulfur cell data is compared to that from our cells with phosphorus-sulfur electrodes.

Cell polarization.—Cell voltage during current flow was measured for the most promising P/S ratio (based on OCV data) and for a Na/S cell. These measurements were made at states of charge for which the equilibrium OCV profiles are flat, and near the midpoint of these "OCV plateau" regions. Because the passage of current in these experiments altered the melt sodium content by only a small

fraction of the sodium composition range spanned by the OCV plateau, the equilibrium OCV did not change during polarization measurements.

The voltages were measured at steady state during constant-current flow. Thus these voltages are a function of current (but not of time) during the measurement period. Plots of steady-state cell voltage *vs.* current were approximately linear in the current range studied, and the corresponding steady-state overpotential/current ratio is reported as cell resistance. From the cell resistance the resistance of the P-S electrode is calculated and compared to that of the sulfur electrode in the Results section.

Experimental

The combination of reactive chemicals and high temperatures required an inert atmosphere and restricted the choice of materials for cell construction. Cell voltage equilibration times ranged from a few minutes to several days, necessitating continuous automated control and data collection.

Materials and Apparatus

Glove box.—A helium atmosphere glove box (Dri-Lab Model DLX-002-D-P glove box equipped with Model M040-2 Dri-Train for oxygen and moisture removal, Vacuum Atmospheres Corporation, Inc., Hawthorne, CA) housed the experiments. Oxygen and water concentrations were controlled to less than 1 and 5 ppmv, respectively, as measured by a trace oxygen analyzer (Model FA31110SA trace oxygen analyzer, Delta F. Corp., Woburn, MA) and a hygrometer (System 580, Panametrics Inc., Waltham, MA). A cylindrical furnace well, 12.7 cm in diameter and 67.3 cm deep, was set into the floor of the glove box to allow heating of the electrochemical cell.

Chemicals.—The chemicals used in this work were sodium metal (99.99%, Lot No. 45690, Noah Chemical, Farmingdale, NY), sulfur (99.9995%, lot No. 25176, Noah Chemical, Inc.), tetraphosphorus trisulfide (P_4S_3, tech. grade, Strem Inc., Newburyport, MA), and graphitized carbon black (GP-3185 Vulcan XC72R, Cabot Corp, Waltham, MA). The sulfur exhibited a sharp melting point and was used without further purification. The sodium was treated with steel wool and titanium sponge at 350 to 400°C to remove suspended and dissolved oxides immediately before charging the cell. The P_4S_3 was sublimed twice, after which the melting range was 171 to 174°C.

Cell.—The cell is shown in cross section in Fig. 1. It consists of a positive electrode compartment containing a molten phosphorus-sulfur mixture and negative electrode compartment containing molten sodium. These compartments are separated and electrically insulated from each other by a solid electrolyte which allows sodium ions to pass back and forth between the compartments.

The electrolyte is a mixture of β- and β''-alumina sintered into a nonporous, closed-end tube (100 mm long, 9.0

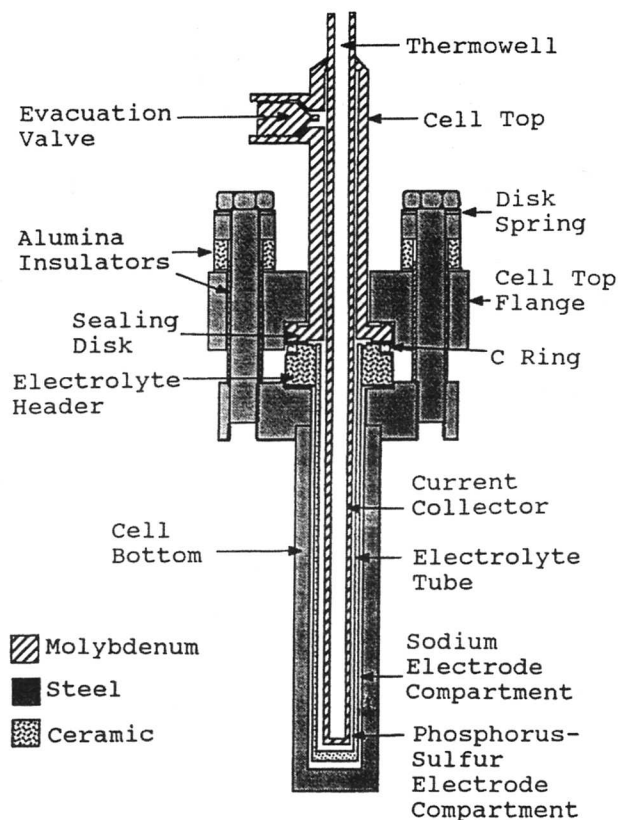---

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Fig. 1. Diagram of the OCV cell.

inner annulus surface is formed by the cylindrical molybdenum current collector (6.4 mm diam). Thus the thickness of the P-S electrode is 1.3 mm. The 1.3 mm gap between the bottom of the current collector and the electrolyte tube is also filled with electrode melt.

A closed-end steel tube forms the cell bottom. It serves as the current collector for the sodium electrode, and is insulated from the cell top by alumina sleeves and spacers and the electrolyte header. The closed-end annular space between the cell bottom and the outer surface of the electrolyte tube is the sodium electrode compartment. The volume of sodium charged to the cell is chosen to ensure that the sodium liquid level is above the positive electrode melt liquid level at all depths of discharge.

Computer control and data acquisition.—The current was controlled and the cell potential was measured by a system which included a galvanostat (Hokuto Denko, Ltd., GPIB potentiostat/galvanostat HA-320G, Hokto Corp., San Dimas, CA), a multichannel (A/D) converter (Model 2240B Data-logger, Fluke, Inc., Fremont, CA) and an IBM AT computer equipped with an IEEE bus interface (Model MBC-488, Keithley-Metrabyte, Inc., Taunton, MA). The computer was programmed to operate the galvanostat as well as record and display the time, temperature, cell voltage, and current. Figure 2 is a diagram of the main components of the experimental system.

Experimental

Cell preparation.—In the inert atmosphere glove box, sodium metal was treated with titanium sponge at 350 to 400°C and transferred into the cell bottom. To prepare the P-S electrode, portions of P_4S_3 (purified as described above), sulfur and carbon black (10 w/o, added to enhance
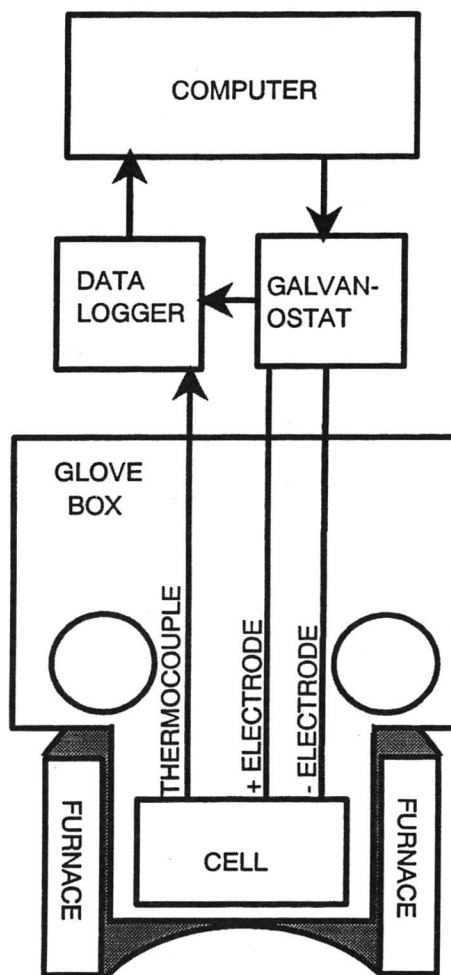
mm id, 10.8 mm od) with an ionic resistivity of 3 to 5 Ω-cm at 300°C (Betalyte BT-10, Ceramatek Inc., Salt Lake City, UT). The electrolyte composition is approximately $Na_2O \cdot 11Al_2O_3$ plus 1 to 2 weight percent (w/o) Li_2O or MgO to stabilize the formation of the more conductive β'' phase.[3,4] The sealing surface is an α-alumina (ordinary alumina) collar (the "header") which is joined to the electrolyte tube with a sealing glass (Ceramatek, Inc.). The effective surface area of the electrolyte is determined by the inside diameter of the electrolyte tube and by the height of the electrode melt level (5.1 to 6.4 mm).

The cell top is constructed of molybdenum and is encircled by an A286 steel collar. Molybdenum was used for corrosion resistance where there is contact with phosphorus and sulfur liquid or vapor, and A286 steel gives the collar torsional strength. The molybdenum part of the cell top includes the current collector (a closed-end tube which also serves as a thermocouple well), a valve which allows evacuation of the positive electrode vapor space after assembly, and a "sealing disk" which is pressed against the electrolyte header to form a joint sealing the positive electrode compartment. This seal requires several design elements. A commercially available high-temperature spring gasket (Part No. 614U5X-0012-2, Pressure Science, Inc., Beltsville, MD) is used in conjunction with high-temperature disk springs (Part No. 50750-A-040-X, Key Bellevilles, Inc., Leechburg, PA) to counter loosening of the seal joint due to thermal expansion. The 3/4 in. od of the disk springs was machined down to 5/8 in. Aluminum foil (0.254 mm thick, 99.5$^+$% pure, Alpha Ventron, Inc., Ward Hill, MA) gaskets are used above and below the C-ring. To minimize external leaks the furnace-well is pressurized to 100 to 170 kPa (gauge) to roughly balance the sulfur vapor pressure in the cell at 500°C.

The geometry of the phosphorus-sulfur electrode compartment strongly affects the results of the cell polarization experiments. The electrode melt in this compartment assumes the shape of a vertically oriented annulus closed at its bottom. The outer surface of this annulus is the inner surface of the electrolyte tube (9.0 mm diam), and the

Fig. 2. Control and data acquisition system.

conductivity) were weighed and placed in an agate mortar, ground together thoroughly, and about 0.6 g of the mixture was transferred to the tared electrolyte tube. The electrode materials were kept molten during cell assembly by heating the cell to 200 to 250°C while the flange bolts were tightened. After cooling, the positive electrode compartment was sealed under vacuum by using the valve in the cell top.

Equilibrium OCV measurements.—The cell was discharged and charged at current densities in the range 5 $\mu A/cm^2$ to 10 mA/cm^2 in measured coulomb increments between which the cell voltage was allowed to stabilize to a drift of ≤ 0.5 mV/h before a reading of the "equilibrium" voltage was recorded.

Reproducibility and accuracy of OCV data.—To confirm that the OCV data are equilibrium values, voltage measurements at a given state of cell charge were made both between periods of cell charge and between periods of cell discharge. During equilibration after charge, positive overpotentials decay, and the OCV drops toward the equilibrium value. After a period of discharge, negative overpotentials decay, and the OCV rises toward the equilibrium value. Thus at a given state of charge of the cell, an OCV measured after charging current has been applied to the cell will be higher than or equal to the OCV measured after a period of discharge. If these two OCV measurements are not equal (charge-discharge hysteresis is observed), the equilibrium OCV lies between them. The voltage range bounded by this hysteresis is the uncertainty in the equilibrium OCV. Such hysteresis was observed in our measurements where equilibration was very slow. Equilibration times of up to nearly two days per point were required to reduce charge-discharge hysteresis to an acceptable level.

By considerations described elsewhere,[2] the uncertainty in OCV measurements was estimated to be ±4 mV in the plateau regions and ±10 mV in the sloping regions where equilibration times ranged up to several days per point. Limited accuracy in measurement of the amount of charge passed (current magnitude and timing) gives rise to an uncertainty in χ_{Na} in the P-S electrode of ±0.001.

Cell polarization.—The current was stepped from zero to a constant value and held there until the cell voltage stabilized, as determined visually with a stripchart recorder. This steady-state voltage was recorded, and the
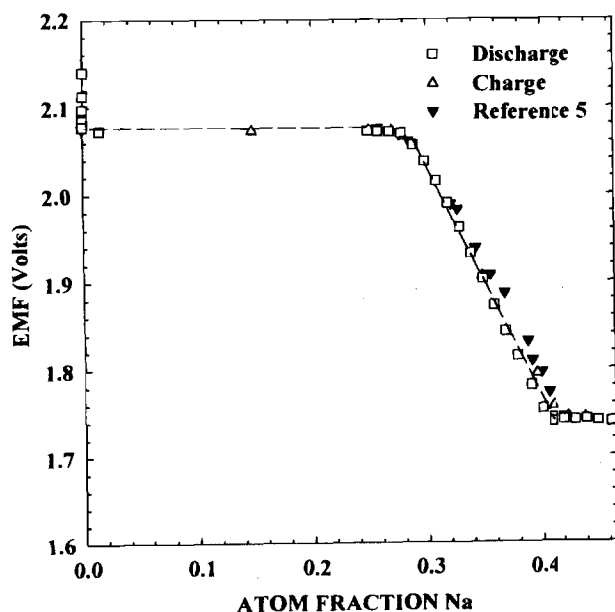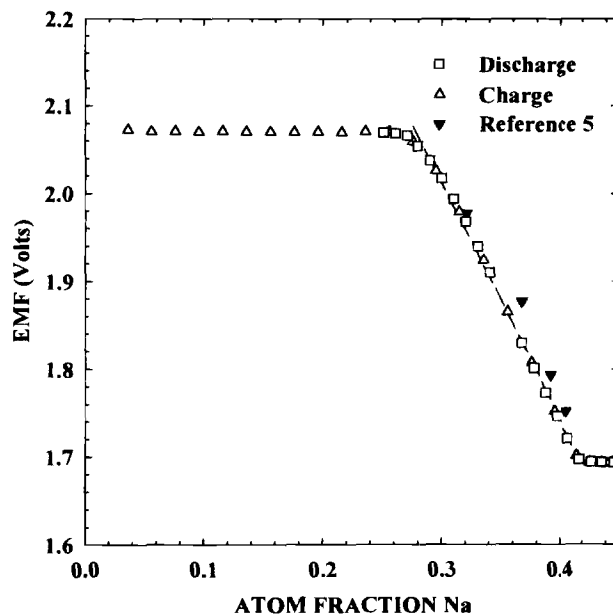
cell was returned to open-circuit. The cell was then allowed to recover to the equilibrium OCV before another constant current pulse of a different magnitude was applied. The magnitude of the applied constant-current ranged from 4 mA/cm^2 to a maximum value, above which the cell voltage during current flow did not stabilize. This maximum current varied from 20 to 72 mA/cm^2 and appeared to depend on temperature, current polarity, and the state of charge of the cell.

In summary, an apparatus and a procedure were developed to make two kinds of measurements on Na/S and Na/P-S cells at 300 to 500°C: (*i*) the equilibrium OCV *vs.* state of charge, and (*ii*) the steady-state voltage at constant current. The purpose of this work was to determine the effect of phosphorus on the performance of the well-studied Na/S cell.
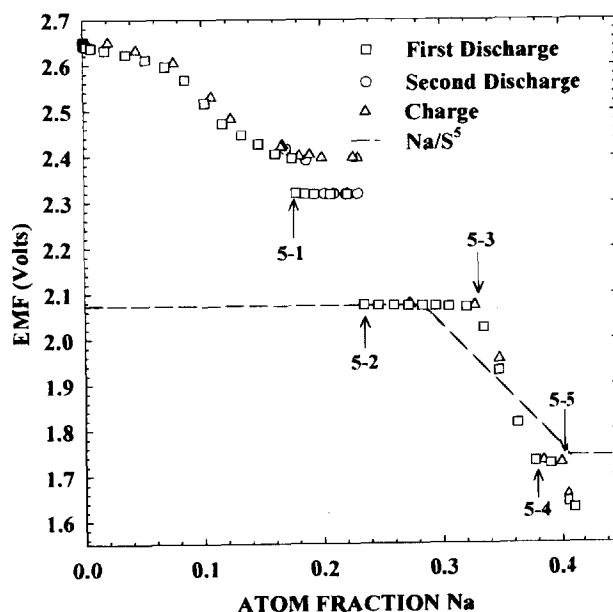
Fig. 4. Equilibrium OCV, Na/S cell, 400°C.

Fig. 3. Equilibrium OCV, Na/S cell, 350°C.

Fig. 5. Equilibrium Cell OCV, P/S = 0.143, 350°C. The numbered break points correspond to phase-field transitions discussed Part II.[8]
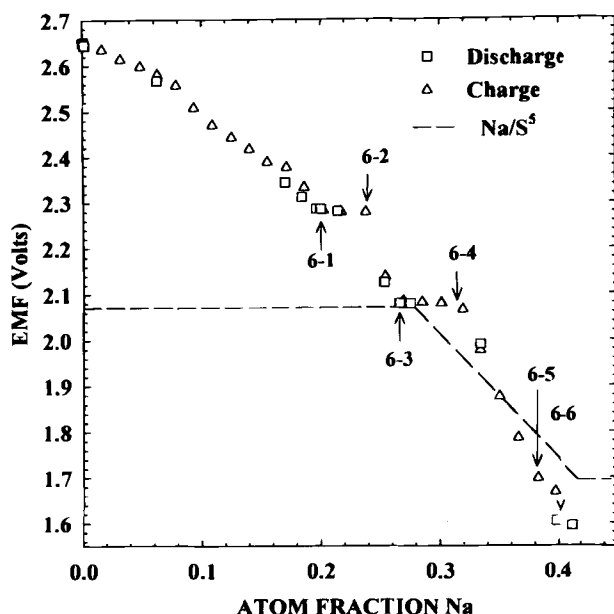
Fig. 6. Equilibrium Cell OCV, P/S = 0.143, 400°C. The numbered break points correspond to phase-field transitions discussed Part II.[8]

Fig. 8. Equilibrium Cell OCV, P/S = 1.17, 350 to 500°C.

Results and Discussion

OCV studies.—OCV measurements were performed using four positive electrode compositions, one of which was sulfur alone. Figure 3 shows that our Na/S cell measurements at 350°C agree closely with those reported in the literature.[5] Figure 4 shows the 400°C Na/S cell data along with the few published data for the Na/S cell at this temperature.[5]

Three phosphorus-sulfur mixtures were investigated at temperatures ranging from 350 to 500°C. The results are displayed along with the OCV curve for the Na/S cell for comparison.

Na-P/S cell with P/S = 0.143.—This experiment continued 50 days until termination by electrolyte failure (cracking). Data were collected at 350 and 400°C. Plots of OCV vs. sodium atom-fraction (χ_{Na}) are shown in Fig. 5 and 6.
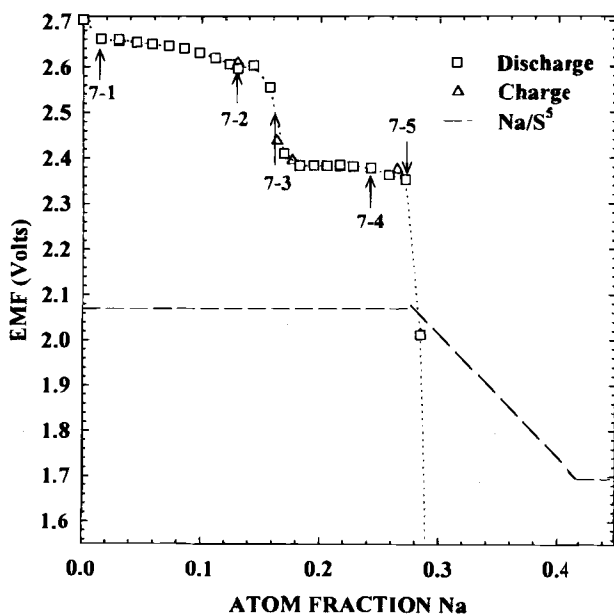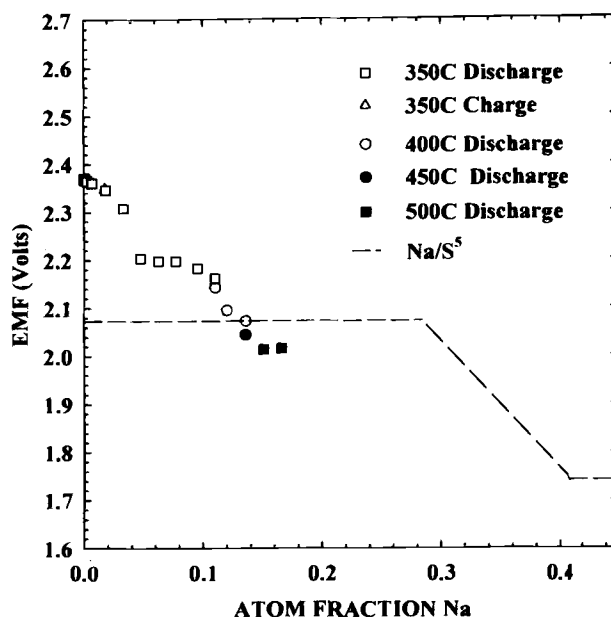
At both temperatures, this cell was discharged until χ_{Na} in the positive electrode reached more than 0.4, which for sodium/sulfur cells is the usual discharge limit. At this point, equilibration times grew to several days and deeper discharge was not attempted.

Exceptionally large and long-lived hysteresis persisted between the charge and discharge data in the plateau region at about χ_{Na} = 0.2 at 350°C (Fig. 5). Two plateaus seem to exist. Equilibration to each of them was rapid, after which cell OCVs were stable for several days. This discontinuity in the rate of equilibration may indicate the development during charging of a phase (perhaps solid) which is very slow to dissipate. At 400°C (Fig. 6) the higher plateau disappears. This higher temperature may be above the melting point of the "solid" phase, or equilibration may have been facilitated by lower viscosity at the higher temperature.

Na-P/S cell with P/S = 0.332.—This experiment was attempted at 350°C, but low discharge rates and long equilibration times, probably due to formation of solids or very viscous liquids, allowed only a few irreproducible measurements which are not shown here. At 400°C the cell discharged more readily up to χ_{Na} = 0.264, after which an abrupt plunge in potential coincided with a large increase in equilibration time making further discharge impractical. These data are shown in Fig. 7. The electrolyte tube failed before higher temperature data could be collected.

Na-P/S cell, with P/S = 1.17.—This atom ratio was chosen because it is very close to a 115°C P-S eutectic in the phosphorus-sulfur binary system.[6] Low discharge rates and long equilibration times at temperatures up to 500°C

Fig. 7. Equilibrium Cell OCV, P/S = 0.332, 400°C. The numbered break points correspond to phase-field transitions discussed Part II.[8]

Table I. Theoretical specific energies.

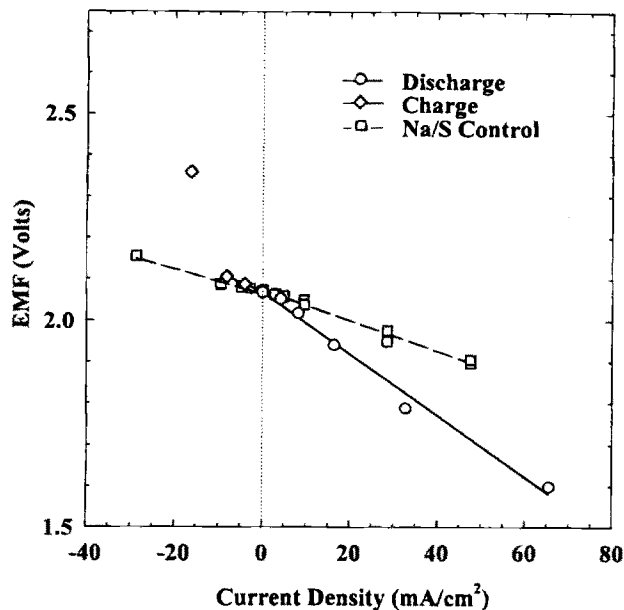| Cell type	P/S (mole ratio)	Temp. (°C)	Sp. E. (W-h/kg)
Na/S[a] (Lit.)	0	350	767
Na/S	0	350	770
Na/S	0	400	758
Na/P-S	0.143	350	825
Na/P-S	0.143	400	820
Na/P-S	0.332	400	571

[a] Calculated from experimental data in Ref. 5.

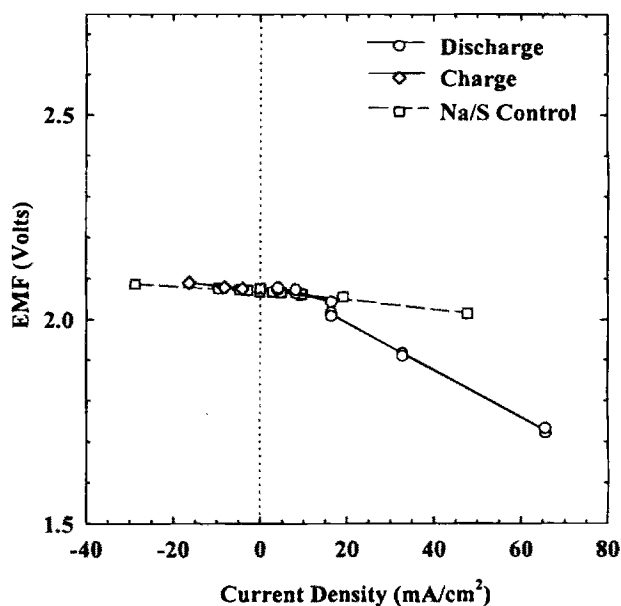Fig. 9. Cell polarization, P/S = 0.143, χ_{Na} = 0.27, 350°C.

Fig. 11. Cell polarization, P/S = 0.143, χ_{Na} = 0.27, 400°C.

again suggest that solids or highly viscous liquids (glasses) were being formed in the electrode as χ_{Na} approached 0.14. The data are shown in Fig. 8.

Theoretical specific energy.—The OCV data were used to calculate the theoretical specific energy by the method described in the Introduction. As shown in Table I, the specific energy of the P/S = 0.143 cell is 7 to 8% higher than that of our Na/S cell. The specific energy of the P/S = 0.332 cell is 25% less than that of the Na/S control cell.

OCV studies: Conclusions about cell performance.—The OCV data indicate that addition of up to 12 mole percent (m/o) phosphorus (*i.e.,* P/S mole ratio 0.143) increases the open-circuit voltage of the cell with respect to Na/S, giving a higher theoretical specific energy. This indicates a possible improvement over the sulfur electrode, and motivated the choice of this P-S mixture for polarization measurements.

Addition to the positive electrode of greater than 25 m/o phosphorus (P/S = 0.332 an 1.17) resulted in increased

Fig. 10. Cell polarization, P/S = 0.143, χ_{Na} = 0.20, 350°C.

equilibration times, from a few hours to a few days. Mixtures of P_2S_5 (P/S = 0.285) and Na_2S are known to form glass-like (*i.e.,* highly viscous) systems.[7] High viscosities in our electrode melts would cause such increased equilibration times.

Cell polarization data.—Figures 9 through 12 are plots of cell voltage *vs.* current density (polarization data) for the P/S = 0.143 experiment at 350 and 400°C, along with the results of similar measurements for the sodium/sulfur cell.

The Na/P-S cell polarization data are markedly different from those of the Na/S cell. The Na/S polarization plots are linear in the current density range studied, with a slight change in slope at zero current. In contrast, much of the Na/P-S cell polarization data are resolved into linear regions separated by voltage discontinuities at both zero current and in the midst of the charge and discharge curves.

The discontinuities at zero current are probably due to the formation of melt layers with sodium concentrations in the ranges of the voltage plateaus shown in Fig. 5 and 6. For example the linear region of the charging curve in Fig. 10 (350°C, χ_{Na} = 0.2) extrapolates to 2.35 V at zero current. Figure 5 indicates that when the χ_{Na} of the P-S electrode ranges from 0.18 to 0.24 the equilibrium open-circuit voltage is 2.32 V. Thus the extrapolated voltage at zero current of the polarization charging curve indicates that the P-S electrode potential during current flow is determined by a melt composition in the range 0.18 ≤ χ_{Na} ≥ 0.24. This is an expected result, since the overall electrode sodium content is χ_{Na} = 0.2. However, the discharge curve extrapolates to 2.09 V, which Fig. 5 indicates is near the equilibrium cell voltage of 2.07 V when χ_{Na} ranges from 0.24 to 0.33. This suggests that during discharge a stable layer of sodium-enriched electrode melt forms, wherein χ_{Na} ranges from 0.24 and 0.33.

A similar phenomen holds at 400°C when χ_{Na} = 0.20, as shown in Fig. 12, which should be compared to the 400°C equilibrium data in Fig. 6. Here a discontinuity occurs in the charging curve between 9 and 18 mA/cm². The data at 3.6 and 9 mA/cm² extrapolate to 2.08 V at zero current, but the data at 18 and 36 mA/cm² extrapolate to 2.27 V. These voltages are close to the 2.08 and 2.28 V plateaus in the equilibrium data shown in Fig. 6. This suggests that during the previous discharge polarizations a layer of melt with a sodium composition (0.24 ≤ χ_{Na} ≤ 0.27) defined by the 2.08 V plateau in Fig. 6 coated the electrode. This layer controlled the potential observed during charge polarizations at up to 9 mA/cm², then was consumed at higher currents and replaced with a layer having a sodium composi-
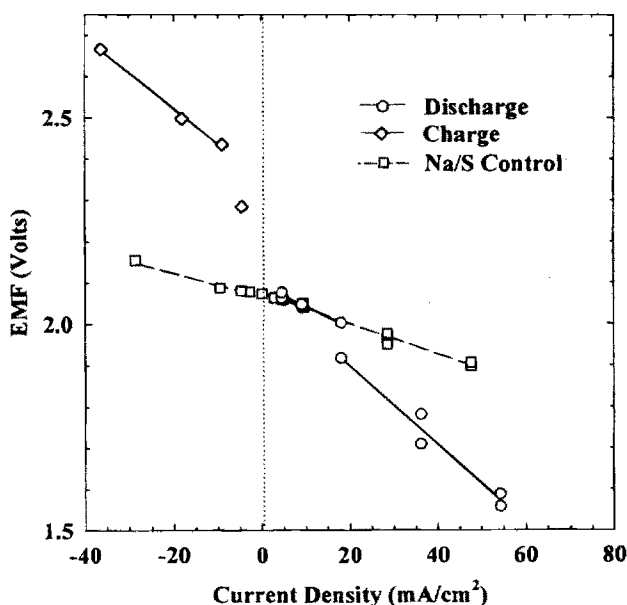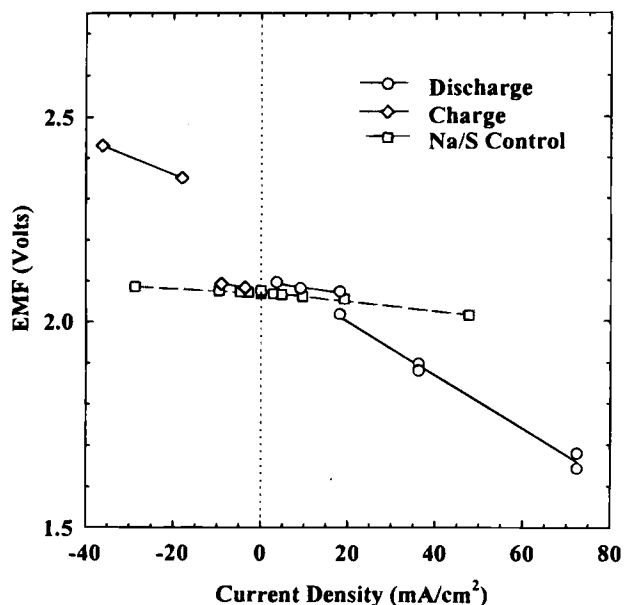
Fig. 12. Cell polarization, P/S = 0.143, χ_{Na} = 0.20, 400°C.

tion in the range of the 2.28 V plateau in the equilibrium data (0.20 ≤ χ_{Na} ≤ 0.24).

The charging polarization curve at χ_{Na} = 0.27, 350°C (Fig. 9) exhibits a sudden OCV rise to >2.37 V at a current density of 16 mA/cm². Figure 5 shows a 2.32 V equilibrium OCV plateau for χ_{Na} ranging from 0.18 to 0.24. This result suggests that a potential-determining melt layer depleted in sodium to within this range had formed in the P-S electrode.

The polarization curve at χ_{Na} = 0.27, 400°C (Fig. 11) shows no discontinuous increase in overpotential with charging currents up to about 16 mA/cm², perhaps due to higher sodium diffusivity at this higher temperature.

The discharge polarizations shown in Fig. 10, 11, and 12 are resolved into two linear regions separated by a voltage discontinuity. The higher current regions have steeper slopes and extrapolate to slightly higher open-circuit voltages than the lower current data, which extrapolate to the voltage of the lower OCV plateaus in Fig. 5 and 6. The voltage discontinuities probably indicate that the sodium content of a potential-controlling melt layer has increased beyond the range of the lower voltage plateau in Fig. 5 and 6. The line slopes and intercepts of the high current data

are probably determined by the interaction of a decreasing sodium activity, increasing ionic strength and changing melt viscosity.

In summary, at the two bulk melt compositions χ_{Na} = 0.20 and 0.27, the cell behaves as if it has a higher open-circuit voltage during charge than it has during discharge. The discontinuities in the polarization curves are probably due to coating of the phosphorus-sulfur electrode current collector with relatively stable layers of electrode melt with a sodium content different from that of the bulk melt.

Cell resistance.—The steady-state polarization data for P/S = 0.143 and the sodium/sulfur control experiment include the effect of internal cell resistance, which causes the polarization plots to have a nonzero slope. This includes ionic resistance in the positive electrode melt and in the electrolyte, and the effect of concentration gradients in the positive electrode. The cell resistance (calculated from polarization data line slopes), and calculated values for the wetted area of the electrolyte, electrolyte resistance and resistivity of the electrode melt are given in Table II.

The cell resistance obtained using a phosphorus-sulfur electrode can be compared to the resistance of the same cell using a sulfur electrode as an indicator of the relative performance of these electrode materials. Table II provides this comparison. The most significant result is that the resistance of the Na/P-S cell was up to four times larger than that of the Na/S cell. Both the Na/S cell and the Na/P-S cell at χ_{Na} = 0.27 show a considerably greater resistance on discharge than on charge, but the resistance of the Na/P-S cell at χ_{Na} = 0.20 is similar on discharge and charge. Two unsurprising trends are that cell resistance decreases with increasing temperature and the P-S electrode has a lower resistance at the higher sodium concentration.

Conclusion

Several characteristics of the phosphorus-sulfur electrode distinguish it from the sulfur electrode. Some P/S mixtures gave higher OCVs and higher specific energies (*vs.* Na) than pure sulfur. The P-S electrode exhibited a higher electrode resistance and increases in resistance at higher current densities. Voltage discontinuities of up to 0.2 V were observed in the polarization curves. Long equilibration times between current steps indicate that the overpotentials were probably determined by concentration gradients. Finally, Fig. 9 through 12 show that within the current density range studied, and for this cell design, the phosphorus-sulfur electrode delivers less power on discharge and requires more power on charge than the sulfur electrode.

Table II. Cell internal resistance.

P/S (mole ratio)	χ_{Na}	h (cm)	S.A. electrolyte (cm²)	R electrolyte[a] (Ω)	Temp. (°C)	Current polarity	I density range (mA/cm²)	R cell (Ω)	R electrode (±0.02 Ω)	ρ electrode (±0.06 Ω-cm)
0 (Na/S ctrl)	0.15	0.51	2.1	0.09 ±0.02	350	charge	0 to 28.7	1.39	1.30	3.47
						discharge	0 to 47.5	1.76	1.67	4.45
					400	charge	0 to 28.8	0.28	0.19	0.50
						discharge	0 to 47.7	0.57	0.48	1.28
0.143	0.20	0.55	2.2	0.08 ±0.02	350	charge	9.0 to 36.2	3.93	3.85	10.50
						discharge	4.5 to 18.1	2.25	2.17	5.92
							18.1 to 54.3	4.33	4.25	11.6
					400	charge	3.6 to 9.0	0.76	0.68	1.86
							18.1 to 36.2	2.00	1.92	5.24
						discharge	3.6 to 18.1	0.67	0.59	1.61
							18.1 to 72.4	0.94	2.86	7.80
0.143	0.27	0.64	2.4	0.07 ±0.02	350	charge	0 to 16.4	1.82	1.75	4.97
						discharge	0 to 65.6	3.10	3.03	8.60
					400	charge	4.1 to 16.4	0.47	0.40	1.14
						discharge	4.1 to 16.4	1.09	1.02	2.90
							16.4 to 65.6	2.42	2.35	6.67

[a] Based on the manufacturer's specified resistivity of 3 to 5 Ω-cm at 300°C. Ceramatek Corporation's limited data at 350°C indicate an insignificant change in resistivity with temperature, compared to the 2 Ω-cm variation in resistivity between electrtolyte tubes. No resistivity data at 400°C is available from Ceramatek.

These polarization studies were performed on half-discharged cells. During open-circuit measurements, equilibration times were observed to increase considerably with depth of discharge. The more highly charged electrode ($\chi_{Na} < 0.2$) has higher open-circuit voltages and faster equilibration rates, and thus may produce charge/discharge performance superior to that of the sulfur electrode.

Cell polarization for only the single P/S ratio 0.143 has been tested. A P/S ratio lower than 0.143 may raise the cell voltage slightly but more importantly it may improve the charging characteristics of the nearly fully charged cell. A small amount of phosphorus may act as a sodium polysulfide or sulfur chain terminator, thereby reducing viscosity, without forming a highly viscous glass-like system which is reported for higher phosphorus concentrations in mixtures with sulfur and sodium.

Acknowledgment

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II. Phase Equilibria

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ABSTRACT

Equilibrium open-circuit cell voltage data from a sodium/β″-alumina/phosphorus-sulfur cell utilizing P/S ratios of 0, 0.143, and 0.332 and a sodium atom fraction ranging from 0 to 0.4 were interpreted to construct ternary phase diagrams of the Na-P-S ternary system at 350 and 400°C.

Introduction

Phase equilibria of high-temperature systems are usually studied by thermal rather than electrochemical techniques. However, equilibrium open-circuit voltage (OCV) data for the sodium/β″-alumina/phosphorus-sulfur (Na/P-S) cell, which were collected primarily to determine its utility for electrical energy storage applications,[1] also contain information about the phase equilibria of the sodium-phosphorus-sulfur (Na-P-S) system. The data are interpreted here to construct tentative phase diagrams of this ternary system at 350 and 400°C. No ternary phase diagram has been published for the Na-P-S system, and only one of several possible pseudo-binary diagrams, the Na_2S-P_4S_{10} phase diagram reproduced in Fig. 1, has rewarded a thorough literature search.[2]

Slope breaks in plots of equilibrium OCV *vs.* electrode composition (OCV plots) occur when phase boundaries are crossed in the electrode mixture. The well-known Na/S cell (of which the Na/P-S cell is a variant) exhibits such behavior, and there are precedents for the use of OCV plots to locate phase boundaries in systems where thermal data are lacking.[3]

Equilibrium OCV data contain information about electrode phase behavior because both are closely related to the Gibbs energy of the electrode melt. The Gibbs energy (G) changes with composition, and phase behavior in the melt is driven by the tendency to minimize G.

The equilibrium OCV is related to G of the electrode melt as shown by the following equations. The Na/P-S cell

can be considered to be a sodium concentration cell for which the Nernst equation is

$$E = -\frac{RT}{NF} \ln \frac{a_2}{a_1} \qquad [1]$$

where E is the equilibrium cell OCV, a_2 is the activity of sodium in the P-S electrode, a_1 is the activity of sodium in the sodium electrode, N is the number of electrons transferred in the cell reaction, R is the gas constant, T is the temperature, and F is the Faraday constant. Since the standard state of sodium is that of the pure molten metal at the cell temperature, $a_1 = 1$. Activity is related to chemical potential by

$$\mu - \mu_o = RT \ln a \qquad [2]$$

where μ_o, the chemical potential of sodium in its standard state, is equal to zero. The definition of the chemical potential of sodium in the P-S electrode is

$$\mu_{Na} \equiv \left(\frac{\partial G}{\partial n_{Na}} \right)_{T,P,n_p n_s} \qquad [3]$$

where P is the pressure, and n is the moles of the indicated component of the melt. Combining Eq. 1 through 3 gives

$$E = -\frac{1}{NF} \left(\frac{\partial G}{\partial n_{Na}} \right)_{T,P,n_p,n_s} \qquad [4]$$

Thus the slope of an OCV plot ($\delta E/\delta n_{Na}$) is proportional to the second derivative of G with respect to sodium content.

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