

AD-A042 541

OFFICE OF NAVAL RESEARCH LONDON (ENGLAND)  
EUROPEAN DEVELOPMENTS IN THE NA/S HIGH TEMPERATURE BATTERY FOR --ETC(U)  
JUN 77 A SOSIN  
ONRL-R-5-77

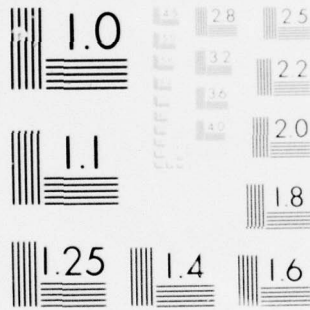
F/G 10/3

UNCLASSIFIED

NL

| OF |  
AD  
A042541





MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

ADA 042541



# ONR LONDON REPORT

ONRL R-5-77

12

## OFFICE OF NAVAL RESEARCH

BRANCH  
OFFICE  
LONDON  
ENGLAND

EUROPEAN DEVELOPMENTS IN THE Na/S HIGH TEMPERATURE  
BATTERY FOR AUTOMOBILE PROPULSION AND ENERGY STORAGE

DR. ABRAHAM SOSIN

13 JUNE 1977

UUC FILE COPY



### UNITED STATES OF AMERICA

This document is issued primarily for the information of U.S. Government scientific personnel and contractors. It is not considered part of the scientific literature and should not be cited as such.

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ONRL-R-5-77 ✓	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) EUROPEAN DEVELOPMENTS IN THE Na/S HIGH TEMPERATURE BATTERY FOR AUTOMOBILE PROPULSION AND ENERGY STORAGE	5. TYPE OF REPORT & PERIOD COVERED	
	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) Dr. Abraham/Sosin	8. CONTRACT OR GRANT NUMBER(s)	
9. PERFORMING ORGANIZATION NAME AND ADDRESS OFFICE OF NAVAL RESEARCH, BRANCH OFFICE LONDON BOX 39, FPO NEW YORK 09510	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 12 11 P.	
11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE 13 June 1977	
	13. NUMBER OF PAGES 15	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report)	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Sodium Load-leveling Electrolytes Sulfur Automobile propulsion Battery Ion transport Alumina Ceramics Energy Storage Electrodes		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The sodium-sulfur battery is a leading candidate for future use in the propulsion of automobiles, vans, buses, and trains and for energy storage and load-leveling by electrical utilities. This report presents a brief description of the fundamentals of the operation of the battery, with indication of some considerations which control its development into an important technological system. The status of the battery development in England, France and Germany is then reviewed.		

DDC  
 AUG 8 1977  
 C

mt

TABLE OF CONTENTS

	page
INTRODUCTION.....	1
UK--CHLORIDE SILENT POWER and BRITISH RAILWAYS.....	5
FRANCE--C.G.E.....	10
GERMANY--BROWN, BOVERIE et CIE (HEIDELBERG) and BATTELLE LABORATORY (FRANKFURT).....	13

ACCESSION for	
NTS	Wire Section <input checked="" type="checkbox"/>
DOC	B.H. Section <input type="checkbox"/>
UNCLASSIFIED	<input type="checkbox"/>
CLASSIFIED	
DISPOSITION/AVAILABILITY CODES	
SP. CIAL	
A	

EUROPEAN DEVELOPMENTS IN THE Na/S HIGH TEMPERATURE BATTERY FOR  
AUTOMOBILE PROPULSION AND ENERGY STORAGE

INTRODUCTION

Among several high-temperature batteries currently under research and development, the sodium/sulfur battery is a leading candidate for early development and utilization. The projected uses of this battery are for propulsion of automobiles, vans, buses, and trains and for energy storage and load-leveling by electrical utilities.

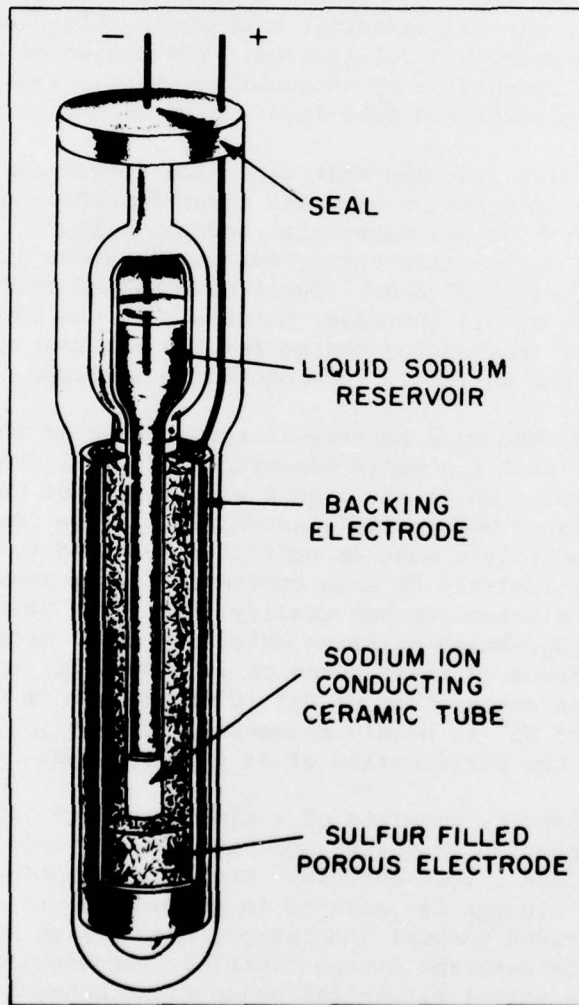
The attractive features that underline development of a Na/S battery are its excellent energy and power densities and its utilization of inexpensive raw materials--sodium, sulfur, and alumina, primarily. The anticipated energy density is about 330 Wh/kg; the power density, about 220 W/kg. These high values follow from the low mass density of all the major materials in the battery, plus the large (negative) free energy change for the reaction which occurs between sodium and sulfur in forming sodium sulfides.

In a sense, the Na/S battery is the inverse of the common lead/acid battery in that the solid electrodes of the latter are replaced by liquid Na and S, while the liquid electrolyte of the lead/acid battery is replaced by a solid electrolyte. Since ion transport through the electrolyte must be sufficiently rapid to allow battery operations, particularly at high currents, it may seem remarkable that any solid electrolyte can qualify. In fact, there are two types of alumina ( $Al_2O_3$ )-based ceramics which are under active production. The  $Na^+$  conductance of these ceramics at 300-350°C, the intended operating range, approaches that of  $Na^+$  in water at room temperature. The transport of  $Na^+$  is highly selective, so much so that the use of alumina for the purification of Na is also under consideration.

The Na/S battery consists of a cluster of individual cells, appropriately connected in series and parallel to yield the design goals on voltage and electrical current. Each cell is physically integral and the entire cluster is packaged in an outside protective container, which also provides thermal insulation. The design of the total battery, the selection of exterior casing material, the requisite number of cells used, the actual electrical connections between cells, etc., are dictated by considerations of application. They are not trivial, but this report will be limited to the more fundamental considerations, namely, those that apply to individual cells.

The configuration of a Na/S cell is shown schematically in the accompanying figure, taken from a presentation by J. T. Kummer and N. Weber, Ford Motor Company. The cell is cylindrical in shape;

flat plate cells have been considered but generally rejected for reasons which relate to cell construction and stresses, rather than any fundamental principle. The figure shows an inner reservoir of liquid sodium with the sulfur electrode external to it; the inverse arrangement, with sodium on the outside is also in use.



The operation of the Na/S battery consists of the ionization of Na atoms with the transport of the resulting electrons through

an external circuit and the concomitant transport of  $\text{Na}^+$  ions through the sodium ion conducting ceramic tube; i.e., the alumina tubing. On passage through the alumina, the  $\text{Na}^+$  ions unite with the available S atoms to form sodium sulfides:  $\text{Na}_2\text{S}_5$ ,  $\text{Na}_2\text{S}_4$ , and  $\text{Na}_2\text{S}_3$ . Which sulfide is formed depends on the state of discharge of the cell;  $\text{Na}_2\text{S}_5$  forms early in the cell operation and  $\text{Na}_2\text{S}_3$  forms near fuel cell discharge. As discharge occurs, the cell voltage changes slowly. It starts at 2.08 V initially and remains there for over 50% discharge. Then an almost linear cell-voltage reduction occurs to termination at 1.76 V.

To maintain the sodium and sulfur (and sulfides) as liquids, operation above  $300^\circ\text{C}$  is required. Higher temperature operations are indicated to achieve increased  $\text{Na}^+$  conductance, as well. However, practical limits set in so that  $350^\circ\text{C}$  is usually taken as a planned operating temperature and  $400^\circ\text{C}$  as an upper limit. The need to operate the battery at elevated temperatures may be viewed as an inherent disadvantage of the Na/S battery and all high-temperature batteries. Balanced against this are the major advantages mentioned earlier.

In the development of the Na/S battery, it is important to keep in mind the application objectives and demands. For propulsion, the power requirements are usually scaled for a Ford Pinto sedan, with a range between 200 and 250 miles. The energy and power requirements for the Pinto point to a battery consisting of about 900 individual Na/S cells. The size of each cell is indicated by the ceramic tubing required--20 cm long, 1.5 cm in diameter, with a wall thickness of about 1 mm.

For load-leveling and energy storage, the battery configuration would be quite different. Thermal efficiency considerations would point to a design in which the total requisite number of cells are clustered into one assembly. Since a 1000-MW power plant would then require over  $30 \times 10^6$  cells, the packing of the individual cells will be determined by maintenance and service considerations, as well as thermal efficiency.

Considering the large number of cells required by only one power plant or the large number of automobiles that might use Na/S batteries for propulsion if electrical propulsion were to replace the internal combustion engine, it is clear that the stakes in the development of the Na/S battery are very large, indeed. Accordingly, it is essential that great attention must be paid to each detail of the battery.

Ford Motor Company holds the basic patents for the Na/S battery. Nevertheless, a number of laboratories in several countries are actively pursuing development of Na/S batteries. The purpose of this

report is to describe some of the work in England, France, and Germany. Not too surprisingly, each of these activities bears many similarities; but there are notable differences, as well.

The heart of the battery is the solid electrolyte--the alumina ceramic. Currently, attention is being devoted almost entirely to two modifications of alumina. In the first,  $\beta$ -alumina, the nominal composition is  $\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3$ , with  $9 \leq x \leq 11$ . The crystal structure consists of Al-O "spinel" blocks, which do not engage in the conductance of  $\text{Na}^+$  but form the structure for the material.  $\text{Na}^+$  conductance occurs in the planes between blocks; in other words,  $\beta$ -alumina is a planar (two-dimensional) conductor. Higher conductance of  $\text{Na}^+$ , by a factor of 2 to 5, can be obtained using a modification,  $\beta''$ -alumina, which is quite similar to  $\beta$ -alumina. In this modification, it is necessary to stabilize the structure, which is thermodynamically unstable, with the addition of about 2 wt%  $\text{Li}_2\text{O}$  or  $\text{MgO}$  (or both). The conductance of  $\text{Na}^+$  ions through the conducting planes of these two structures is related in part to its small ionic size:  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$ , located in the same column of the periodic chart, show little conductance. But size is not the full story; if it were,  $\text{Li}^+$  would be expected to be even more mobile, contrary to observation. The more subtle factors which limit  $\text{Li}^+$  mobility have been explored by R. Huggins and others.

The use of  $\beta''$ -alumina is more general at this time. In these cases, the actual structure frequently consists of a  $\beta$ - $\beta''$  mixture.

To bring these ceramics to application in batteries requires attention to a host of questions. What modification of alumina and what chemical composition will, in fact, produce the optimum  $\text{Na}^+$  conductance? How should the alumina be processed? Extrusion, isostatic pressing, sintering, electrophoresis, etc., have all been examined. How long can the tubing be made and how thin can the wall thickness be fabricated? What are the mechanical and corrosion properties of the tubing? What about cost?

Despite the central importance of the electrolyte, the achievement of a battery requires consideration of many other factors. Pure sulfur is not an electronic conductor. The formation of neutral sodium sulfides is required for operation of the battery and this requires the passage of electrons from the electronic circuit. How does one effect this conductance? One possibility would be to dope the sulfur, however, the more accepted approach is to fill the sulfur electrode with graphite felt, which serves to conduct the electrons. What material should be used as the outside cell-container material? Here one needs light weight (for propulsion), no corrosion problems, and economy in selection and fabrication.

A complete description of all of the considerations which will eventually determine the success of the Na/S battery is beyond this report. It is merely hoped to provide herein a panorama of the developments in Europe and, at the same time, furnish an insight into the problems of transforming a most promising scientific concept through its engineering and development stages.

#### UK--CHLORIDE SILENT POWER AND BRITISH RAILWAYS

For the last three years, British activities toward the development of an advanced battery have been organized into a triumvirate arrangement between Chloride Silent Power, Ltd. (CSP), the British Railways Board (BR), and the Atomic Energy Research Establishment (AERE). In addition, "one-man" research efforts which contribute to this development are carried out in a few universities. Each member laboratory has its mission outlined. However, there is a purposeful overlap of activities and even a residue of competition to spice the work.

In this arrangement, CSP retains the greater portion of the fundamental work. The role of BR is somewhat more end-product related. The AERE (Harwell) plays an advanced technology role, which includes providing many of the services that Harwell is particularly capable of, or which might be prohibitive for smaller research institutions, such as CSP and BR. The funding of the research in the case of CSP is 51% internal and 49% through the Central Electricity Generating Board; BR has been supported in its work 100% by the Department of Environment; this support is being transferred to the Department of Transportation. The effort at Harwell is government funded through the Department of Energy.

The work of this triumvirate is exclusively devoted to the development of the Na/S high-temperature battery. There is little or no other activity in the UK in the area of high-temperature batteries other than the Na/S battery. This "eggs-in-one-basket" commitment resulted from consideration of a number of factors. From a technical vantage point, the British felt that Na/S represented the system which appeared most promising among the available alternatives. A similar decision would almost certainly be reached today, based on the opinions of the researchers at CSP and BR; however, they are watching with interest, if not concern, at the development of alternatives, particularly the Li/metal-sulfide cell.

A second consideration which pointed to the development in Britain of the Na/S battery is the fact that both CSP and BR have been involved with this battery for about a decade. It is also true that the potential of this battery for its intended applications is viewed as established by the investigators and, generally, by those to whom they report. Finally, there is the financial consideration. It would

be a major burden for Britain to attempt to develop an alternative high-temperature battery system concurrently with Na/S development.

Nevertheless, the economics of the battery retain considerable uncertainty for the British. In the US, energy storage and load-leveling are major application goals, as they had been in the UK until quite recently. Two events have modified the British position-- the OPEC oil embargo and North Sea oil exploration. The embargo resulted in substantial reduction in consumer demand for electrical power, enough so that Britain currently possesses excess electrical capacity for base-line power and sufficient for peak-power handling. The situation is complicated by the British desire to retain an active nuclear development in order to maintain an important position in a worldwide reactor market that is marked by gross uncertainties. The expectation of rapid realization of North Sea oil imports further eases any crunch that pointed to a dire early need for vast energy-storage systems.

The transportation application for the Na/S battery is, therefore, the more likely one for early realization in the UK. This is the obvious intention of BR, and the moment of decision whether to go into production of batteries for rail use is approaching. In this regard, the British position with respect to the Na/S battery is distinct from that of other nations; a prime customer has been identified, and the development of the battery is directed substantially toward this customer's requirements. In contrast, in the US the potential application of the Na/S for transport (notably automotive) is less developed and less certain.

The use of Na/S batteries in the near future for transportation other than railways and possibly buses is limited in the UK. With the tight financial situation, governmental interest centers more on conservation of sterling than conservation of natural resources. North Sea oil provides Britain with an energy supply that is less polluting than coal. Furthermore, the cost of oil should stabilize for Britain, making the competitive finances of Na/S more difficult.

CSP is a small member of Chloride Group Ltd., a company with capitalization of over £100 million. Over 10% of all the batteries produced in the Western nations are produced by the Chloride Group, which possesses holdings throughout the world. The 40 or so employees of CSP are housed in a modest new building in Runcorn, Cheshire, in the industrial corridor between Liverpool and Manchester. A two-hour drive separates CSP from BR in Derby. The manager of CSP is B. Halliwell and I. Wynn-Jones is their chief scientist. Wynn-Jones has been with the Na/S battery project since its inception, originally at the Electricity Council's laboratories in nearby Capenhurst.

The ultimate goal of CSP in Na/S battery development is a ten-year life; however, initially, they would settle for less. In fact, they currently have single cells that have been in 3-cycle per day operation for four years. The cells are designed to allow for regenerative braking, which requires the capacity for a large charging current. The obvious advantage in the use of regenerative braking is the economy of transforming a portion of the kinetic energy of the vehicle into stored energy in the battery, rather than merely dissipating it as heat. This is generally estimated to afford a 10% savings. There is a more subtle advantage in the employment of regenerative braking in the case of road vehicles, however: It provides braking when the driver's foot is off the accelerator pedal in much the same fashion as in the contemporary automobiles equipped with internal combustion engines. This is expected to help win driver acceptance. Other features of the battery currently receiving attention are fuel gauges. It is still undetermined whether a "power-used" or a "cell-voltage" gauge is best.

In addition to trains, one of the early market targets for battery use may be electric city buses. Chloride Group developed the "Silent Rider" bus powered by lead-acid batteries. The situation with regard to this bus and a somewhat similar one developed by the British Department of Industry was reviewed previously (*ESN* 30-11:506). In addition, Chloride Group has developed the "Silent Karrier" for city-center goods deliveries. These vehicles have demonstrated to the satisfaction of the Chloride Group management the developmental potentials of battery-driven vehicles of selected types. The role of the Na/S battery in this development program is clear. Lead-acid batteries store about 100 kWh of energy; the capacity of the projected CSP Na/S battery is approximately 250 kWh, and the weight advantage lies with the Na/S battery.

CSP's areas of battery research and development include the Na electrode, the S electrode, the alumina electrolyte, the battery container and seals. The primary effort is concentrated on the electrolyte. CSP is developing a mixed  $\beta$ - $\beta$ " alumina system, apparently similar to the ceramic system in the Ford Motor Company's battery program in the US. CSP regards the details of their alumina tube fabrication as one of their key competitive capabilities; consequently, visitors are not admitted to this laboratory and discussion is proprietary. It is likely that the technique is similar to one developed at the University of Utah, a pass-through sintering operation. Most of the ceramic development in the past centered on a material with an electrical resistivity at 300°C (standard reference temperature) of about 10 ohm-cm. Improvements in the electrolyte have reduced this to about 5 ohm-cm. Alumina tested at 12 ohm-cm have shown excellent shelf-life characteristics; CSP is hopeful that alumina with the more improved conductivity will be equally acceptable in shelf-life. CSP

has also investigated a  $\beta''$ -seeding technique reported by the University of Utah to provide better homogenization. This seeding technique has worked in CSP's hands also, but they have not yet achieved adequate mass density.

A fairly detailed optical and scanning electron microscope study has been made by G.J. May and S.R. Tan on the influence of microstructural defects on the tensile strength of  $\beta$ -alumina. The rationale of the study is that the mechanical deterioration and eventual cracking of the solid electrolyte has probably been a prime consideration in the development of the battery for a number of years, although several laboratories have reached a sufficiently advanced state that this problem seems largely solved. The inherent flaws which threaten the ceramics include voids, foreign inclusions, microcracks, and large grains. May and Tan find that the observed tensile strength values obey a Weibull distribution, common to other engineering ceramics. Grain size is particularly important. They conclude that the optimal alumina, for mechanical considerations, should have a uniformly fine-grained structure and be free of defects that are greater in size than about 10  $\mu\text{m}$ . The achievement of such an electrolyte would ensure a more homogeneous current distribution which, in itself, would contribute to mechanical strength and cell reliability.

The electrolyte tubes developed by CSP have grown progressively larger. An early geometry was 1 cm diameter x 20 cm long. More recently, the tubes are 3 cm diameter, 20 cm length, and 1.5-mm wall thickness. CSP feels sufficiently confident to set their next goals: 3 cm diameter, 62.5 cm length, and 1.5 mm thickness. They have also established these tolerances: less than 0.1-mm variation in length between tubes, roundness to 0.1-0.2 mm, straightness to 1.5-2 mm over the entire length.

CSP has performed elemental analysis to determine the extent of contamination of the ceramic introduced by other cell elements, particularly the container material. Their results indicate no such contaminants in the prototype cells. Nevertheless, they have reversed an early design and now place the Na on the outside of the alumina tube and the S on the inside to minimize even potential contamination. They are currently considering the possibility of going from a circular cross-sectional battery cell to square cross section. The circular configuration is simpler and more economical, but CSP feels that the square array may be safer, in the event of automobile collisions, for example.

The studies of the S electrode center on wicking. Transport of  $\text{Na}^+$  away from the electrolyte into the S-electrode requires good wetting of the alumina. The wetting between sulfur or sulfides and the graphite felt is equally important, and wicking is the manifestation

of this wetting. In order to study wetting, CSP uses, in a simple experimental configuration, a carbon felt roll partially dipped into molten S, forming one side of a balance. As the S wets the felt and climbs, the balance monitors the uptake. A more "scientific" study at CSP by M.P.J. Brennan has been concerned with the electrode kinetics of carbon electrodes in various polysulphide (e.g.,  $\text{Na}_2\text{S}_{4.3}$ ) melts. He examines the current response to a linear potential sweep for different sweep rates. The sweep patterns show a region in which polysulphides are oxidized to higher polysulphides and a region in which a film of liquid sulphur forms on the electrode. In the latter region, the electrode can be polarized beyond the point at which sulphur formation starts, without appreciable hysteresis in the return sweep. Brennan attributes these observations to the formation of sulphur rings, perhaps as high as  $\text{S}_8$ .

Wicking at the Na electrode is of equal importance. CSP uses a stainless steel mesh in contact with the alumina to produce Na wicking. In these studies, the resistance of a Na/Na test cell is measured during current passage. In time, there is a transfer of Na from one side of the alumina tube to the other so that the Na pool level on the outside drops continuously. Despite this, the wicking is sufficiently successful that the cell resistance remains essentially constant until about 90% of the active outside tube length is uncovered. The remaining 10% is associated with the rounded cap termination of the tube. The steel mesh is no longer in contact with the tube here but does extend into the Na reservoir. The cell resistance rises somewhat abruptly when the level becomes this low. The studies indicate the success of a steel mesh wick in realizing full cell capacity.

A second proprietary area at CSP is the sealing of the alumina tubes to glass. CSP is dealing with stresses in these seals since cracking of seals poses a major factor in potentially limiting cell lifetime.

CSP conducts a very large testing program on Na/S cells. Their facility allows for the simultaneous operation and monitoring of 300 cells. A comprehensive computer-logging, data-reduction, and readout system has been installed and is largely complete. The operation of the tests is automatic; charge and discharge cycles are carried out for the entire bank of cells together and a test is stopped on any cell in which the open-circuit voltage drops to less than 1.7 V.

The operations at BR are a bit smaller in size, with about 25 personnel; however, they obtain services from supporting groups at their Central Laboratories. They, with CSP, are, of course, looking

toward longer alumina tubes, but currently are working on 16 cm lengths. Unlike CSP, they are producing their tubes in a batch process, encapsulating in MgO to minimize Na<sub>2</sub>O loss during sintering; they can produce about 20 tubes in a single batch, occupying a sintering furnace for one day to include heat-up, sintering, and cool-down times. Their ceramic tubes look very good, and BR confidently state that they have solved corrosion and humidity problems. They attribute their success to good ceramic production techniques. Their large spray-drying system for producing alumina powder is a particular source of pride. The spray-drying capacity is 10 kg per day, which would yield about 80 tubes. They have recently completed a six-week production cycle, including tube fabrication.

BR's activities, under the direction of J.L. Sudworth, are expected to progress along the following schedule. In early 1978, they expect to test a 50-kWh battery composed of 300 cells. The cells will be 100-A h cells (the current cells are 40-A h cells). In 1979, they will test a 400-kWh battery, the nominal size required on the railways. These tests should then allow BR management to make its decision concerning scale-up for production. No mass production facility has been formally considered.

Railways are, by tradition, extremely safety conscious. As a result, BR has required, as a design consideration, that the Na be immobilized within the battery in case of accident. Glass and metal spheres were used previously for Na immobilization. Attention currently appears to have passed to full battery-containment of any rupture, avoiding the capacity penalty that spheres might incur. To test this concept, BR has used an old war-time bomb shelter and exploded cells within it. A typical configuration is a cluster of seven cells in a close-packed configuration; i.e., a central cell surrounded by six outer ones. The center cell is caused to explode and the effects on the others observed, with the entire arrangement subject to differing conditions. The temperature pulse that results from the rapid mixing of Na and S through an explosion is recorded. BR is delighted to report that the effects of such precipitous scenarios are so slight that it is difficult to find any visual effects either on post-inspection or in the study of the characteristics of the cells that were not exploded.

FRANCE--C. G. E.

Prime responsibility and the major effort for the French development of the high-temperature Na/S battery lies with the Compagnie Générale d'Electricité (CGE) in their laboratory in Marcoussis, a rural suburb about 25 miles south of Paris. This laboratory, under the direction of Dr. J.P. Dumas, is the Centre de Recherches for CGE, so that the Na/S battery development is only one of the activities

underway there. One gathers the impression from visiting the laboratory and reading CGE literature, however, that a good deal of pride is involved in this work, which has been in progress since 1968.

The French strategy is notably different from that of the British, Americans, and Germans. The French have chosen to develop the  $\beta$ -alumina solid electrolyte (not  $\beta''$ ), with the accompanying penalty of lower  $\text{Na}^+$  conductance, by about a factor of two. In addition, the "green-state" fabrication method that the French are using is electrophoresis, a method that has been used by few others (e.g., General Electric, US) in this application. So it will be interesting to observe the progress of these parallel efforts to see which path leads to an accepted battery most expeditiously and effectively.

In fact, CGE did consider  $\beta''$  and, to this end, experimented with additions to their alumina at an earlier stage. The opinion, at that time, was that such additions were largely responsible for the poor performances they then obtained. The alumina emerged with a spotted, dark color that disappeared with the deletion of additives. Li and K were particularly suspect; Mg was less suspect. CGE investigators believed that trivalent additives might be acceptable, but chose additive elimination, instead. The subsequent avoidance of these problems at other laboratories using  $\beta''$ -alumina makes this analysis less certain. Similar experiences have been obtained with regard to electrolyte corrosion and cracking. Thus, it is possible that many of the problems that CGE sought to avoid by choosing  $\beta$ -alumina instead of  $\beta''$ -alumina have been minimized or eliminated by other  $\beta''$ -alumina artisans.

Stabilization of  $\beta''$ -alumina requires additions, such as MgO or  $\text{Li}_2\text{O}$ ; none are required in the case of  $\beta$ -alumina and the economies in processing are considerable. There was some hope that diffusion, in the sintering treatment, might be simpler, but it is not clear that experience has borne this out. Standard CGE treatment is sintering at about  $1800^\circ\text{C}$ , but they also use a 10-hour treatment at temperatures between  $1600$  and  $1700^\circ\text{C}$  and are experimenting with "rapid sintering," in this case two to three hours.

The decision to proceed with  $\beta$ -alumina may fit the CGE purposes well. Their market goal is energy storage. Little attention has been given to vehicle propulsion applications. Apparently, the automobile producers in France have failed to respond to the possibility of Na/S-propelled vehicles. For energy storage applications, the reduced electrical energy conductivity of  $\beta$ , compared to  $\beta''$ , is a less important consideration.

The heart of successful electrophoresis lies in choosing the best slurry solution medium and providing a reactive powder. CGE

is still working on both, with considerable success already. Media tend to be organic liquids, and CGE regard its current favorites as proprietary. Reactivity is an area of more concern; but the performance is quite good as their electrolyte-tube characteristics demonstrate. The tubes are beautifully white, very smooth, and have wall thicknesses as low as 0.2 mm (although this is not the standard CGE wall thickness).

The treatment starts with the preparation of reactive alumina and its deposition on a stainless steel mandrel by electrophoresis. The deposit is dried on the mandrel in an oven and the tubing is simply slipped off the mandrel, an act that I still find somewhat amazing, considering the state of the ceramic, the dimensions, etc. The free-standing tube is pressed isostatically; the last step is the sintering treatment. Laboratory tubes have been sintered in closed holes in large blocks of alumina that were previously produced. These holes were drilled for the insertion of the pre-sintered electrolyte tubing. This is, of course, a very costly business, a fact that CGE realizes. They are moving to alternative encapsulation geometries.

There has been some opinion that this process is too costly, particularly with the requirement for a large number of stainless steel mandrels with requisite surface smoothness. CGE has performed an economic analysis and concluded that their processing methods and competitive ones are essentially equivalent in cost. They can produce 1 tube per minute in electrophoresis.

Lifetime for batteries in storage applications must be high, and CGE's best records here are a Na/S cell that has been run in a glass enclosure for 6000 hours and a cell in a metal enclosure for 4000 hours.

Production of the ceramic electrolyte for the Na/S battery has received major attention. The rest of the battery is still in the design state and a demonstration system is under construction. This deliberateness in approaching a full battery configuration is dictated somewhat by the French system itself. CGE is very interested in proceeding rapidly. They have transferred Y. Lazennec to Ceraver, a wholly-owned ceramic production concern, to set up electrolyte production, and SAFT, another subsidiary, would be the logical battery producer. Yet, the French strategy is not well-defined. Presumably, the Na/S batteries will be used in power substations that are small compared to those in the US. The advantage of storage battery systems tends to grow with size. This consideration, along with uncertainties in the entire French energy strategy, have precluded firm decisions. A further complication is the competition to Na/S batteries from the air/Zn battery, also under development at CGE.

GERMANY--BROWN, BOVERIE ET CIE (HEIDELBERG) AND BATTELLE LABORATORY (FRANKFURT)

It is generally helpful to draw analogies between the less familiar and the more, even if such analogies suffer from lack of accuracy. In this vein, Brown, Boverie et Cie (BBC) is a European analog of the Westinghouse Electric Corporation in the US. Electrical power is the main business thrust.

Somewhat over three years ago, BBC Heidelberg made an evaluation of competing energy-storage systems. Their conclusion was that the high temperature Na/S battery appeared most attractive for their attention. The reasons are common: the main materials which comprise the battery, Na, S and alumina, are very plentiful and basically inexpensive. The technology to produce the battery looked feasible. And, somewhat peculiar to BBC, their experience was applicable: they had spent considerable effort on the development of  $ZrO_2$  electrolyte for fuel cells and, in the process, accumulated significant experience in ceramic processing. Therefore, the transfer of this experience to the fabrication of the crucial alumina electrolyte in the Na/S battery seemed reasonable. Accordingly, a union was developed in which BBC is charged with overall responsibility, battery design, assembly, and electrolyte research. Battelle Institute (Frankfurt) is the other major laboratory involved. Prof. H. Felzer (Univ. Konstanz) is the structure specialist, using his extensive background in x-ray analysis, and Dr. A. Divecek (Kernforschungsanlage, Jülich) is most concerned with the sulfur chemistry, mainly the formation and characteristics of the several sodium polysulfides which form during battery operations. In addition, Friedrichsfeld GmbH (Mannheim), a ceramic-processing firm, is tooling-up to take over larger scale electrolyte processing after a period during which the technology is transferred from BBC to them; Friedrichsfeld's experience has been mainly in structural ceramics, and technical ceramics pose a new challenge to them.

Among the several groups and countries involved in the Na/S battery development, BBC is a reasonably late entry. Understandably, their efforts to date have been largely directed to "playing catch-up," but some of their results are interesting and impressive. Perhaps the most interesting one is the BBC success with MgO additions to the  $\beta$ -alumina electrolyte. Whereas other laboratories have reported limited success with MgO, compared with  $Li_2O$ , BBC has had considerable success with MgO as evidenced by the following. They have achieved an electrical (ionic) resistivity at  $300^\circ C$  of 5 ohm-cm or less, occasionally down to 3 ohm-cm; fabricated tubes with wall thickness down to 0.7 mm in short lengths and 1.5 mm in tubes with longer lengths (20 cm) and diameters of 1 in.; achieved densities 98% of theoretical; and, perhaps most impressive, operated Na/Na

test cells in an overflow arrangement for more than 6000 A h cm<sup>-2</sup> at a current density of 0.9 A cm<sup>-2</sup>, about as successful as performances recorded at more experienced laboratories.

The BBC successes with MgO-alumina are even more impressive when one considers that they have used MgO additive amounts varying between about 1.5 and 3.3 mole % and found little difference. Their current belief is that too much importance has probably been attached to composition itself. Instead, the microstructure would appear to be the more dominant consideration. However, there is a strong tie between structure and composition--a tie which diverts attention to composition, a quantity more simply monitored. The processing treatment needed to achieve an optimal structure depends on composition, so that a full structure/processing study may be required before any composition can be judged as undesirable.

Some other features of the BBC electrolyte are as follows: The phase composition is, typically,  $\beta$ "-alumina with 10-15%  $\beta$ . Degradability due to water uptake is minimized by storing their fired alumina tubes at over 100°C and by higher sintering temperatures. However, Na loss becomes stronger at higher temperature. To date, BBC has countered the Na-loss problem by packing the green alumina tubing in Na<sub>2</sub>O-doped alumina powder. This treatment is successful but time-consuming and, therefore, expensive. BBC is working toward methods to avoid the use of embedding powders.

To date, the flowability of the BBC powders has been poor. They have now gone to a more free-flowing one. This is a crucial aspect for large-scale production. The fine alumina particle size in the free-flowing powder enhances the tendency for water uptake, unfortunately.

In addition to attention to the solid electrolyte, BBC has examined other aspects which contribute to cell performance. The geometry of the graphite cell in the S compartment can be important. The viscosity of S and the polysulfides which form during operation, as well as immiscibilities between the sulfides, has suggested that the felt may be improved by holes located next to the electrode. The holes are about 4 mm in each dimension. Measurements of cell voltage during a charge/discharge cycle do indicate improvement with this modification. The BBC interpretation of this problem is that, without the holes, sulfur droplets are formed at the electrolyte surface, giving rise to an electrically insulating layer that defeats the purpose of the graphite felt. In still another development, BBC added less than 1 mole % of Se to the sulfur, to decrease the viscosity of the melt. The improvements realized here are comparable with those effected by the felt geometry method.

Of considerable concern has been the observation of Si on the ceramic tube wall after extended cell cycling. The source of the Si is the stainless steel current collector for the sulfur compartment; stainless steel is a candidate for battery containment material.

Overall, BBC is optimistic about the Na/S battery. Their plans call for the development of a small demonstration battery by the end of 1977.

The history which led to Battelle's involvement is interesting--it started some 15 years ago with clothes-washing. Battelle was engaged in looking at the processes in the family washing machine which center around clay adhesion to fabrics. From this introduction to clays and clay particles which might be considered the precursor for ceramic bodies, Battelle progressed to fuel-cell research (now largely discontinued) including the solid electrolyte of fuel cells, and arrived about 3.5 years ago at the Na/S battery project, with its emphasis on a  $\beta$ -alumina electrolyte. Nevertheless, main ceramic research is the province of BBC; Battelle has been charged with cell operation. Corrosion has been a matter of concern for Battelle. In order to assess the corrosion of the battery-container material, a group under H. Binder, including R. Knoedler and W. Baukal, has assembled simulating sandwich arrangements consisting of graphite/ $\text{Na}_2\text{S}_4$  in graphite felt/metal specimen. The specimens consist of Cr-Ni steels (both austenitic and ferritic), carbon steels and some proprietary iron-free super alloys. The cells are run under a current flow, to simulate operating conditions. Typical corrosion rates reported in this study are about 5  $\mu\text{m}$  in 1000 hours in the best cases, namely proprietary superalloys. By comparison, the carbon steels may show several hundred  $\mu\text{m}$  decrease in thickness.

The most promising recent development at Battelle for the Na/S battery is the adaptation of a stainless steel felt for immobilization of the liquid sodium. The felt is provided by the Brunswick Corp. (Skokie, Illinois) and the Württembergische Metallwarenfabrik (Geislingen, W. Germany). The porosity is between 80 and 90%, a value which certainly is not apparent to the naked eye. The use of any immobilizer involves a loss in capacity in the cell plus an extra economic penalty in itself; balanced against this are beneficial features of safety in case of crash and the opportunity to use the Na/S in a horizontal configuration, as design considerations for automotive application might require. Battelle's study of the felt shows good cell operating characteristics provided the felt makes a close contact with the alumina electrolyte. If the felt is more removed from the electrolyte, there is a competition in wetting by the sulfur between the felt and the alumina.

Perhaps the major problem Battelle faces is that financial support has been interrupted for the Na/S project, with a concomitant drop in research effort.

