PILOT PLANT DEVELOPMENT OF β''-ALUMINA ELECTROLYTES AND RUTILE CONTAINER/CURRENT COLLECTORS FOR THE SODIUM–SULFUR BATTERY

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This program was carried out under Phase III of the Ford–DOE Sodium–Sulfur Battery Development program and work is continuing under Phase IV.

The Phase III objectives were: (1) pilot plant development for producing β''-alumina; (2) delivery of β''-alumina electrolyte assemblies to meet the needs of the cell development program; (3) development of conductive rutile containers and current collectors for sodium–sulfur cells.

A 12 000 square foot pilot plant and testing facility, including space for electrolyte assembly production, quality control and testing, was placed into operation. Major equipment, which was purchased, installed, and placed into operation includes: (1) a Patterson ball mill; (2) a Bowen spray dryer; (3) a Loomis ($\leqslant$275 MN/m^2 (40 kpsi)) wet-bag isostatic press with an air compressor; (4) a Despatch bisquing furnace; (5) quality control facilities including (a) an Instron testing machine; (b) metallographic polishing facilities; (c) an optical microscope. Three major pieces of equipment were designed, constructed, and placed into operation. These included: (1) a calcining furnace presently capable of producing daily up to 240 kg of zeta-process powder; (2) an elevator batch sintering furnace (Super Kanthal heating elements) capable of sintering horizontally at least 50 (34 mm o.d. × 250 mm long) β''-alumina tubes on a daily basis; (3) a sodium–sodium cell testing facility.

Significant processing developments included: (1) the horizontal sintering of 33 mm o.d. (250 mm long) electrolyte tubes in ceramic (α-alumina) Vee-setters which reduce considerably the ovality incurred in unsupported sintering; (2) the sintering of tubing in pre-tested (Na_2O) α-alumina carrier tubes without the use of platinum (Na–Na cell tests indicate acceptable radial resistivities (~5 ohm cm at 300 °C) and excellent endurance ($\geqslant$1000 A h/cm^2); (3) the possible economical use of platinum in sintering as a re-usable liner in an α-alumina carrier tube; (4) the continuous, unencapsulated sintering of 15 mm o.d. (200 - 300 mm long) tubing; (5) the development of a dry ball milling procedure for Meller-based powders.

As of June 1, 1978, when the pre-pilot plant at the University of Utah was shut down and equipment was transferred to Ceramatec, 681 β''-alumina tubes of various sizes, unsealed or glass sealed to α-alumina headers, had been delivered or fabricated since the inception of the DOE contract in 1975. By the end of Phase III (28 February, 1979) approximately 250 additional electrolytes had been delivered from the pilot plant.

This work is being continued under subcontract to Ford Motor Company as part of Phase IV of their DOE contract.

The objectives of this project include: (1) the development of β''-alumina electrolyte manufacturing processes including those based on low-cost starting materials; (2) the production of standardized assemblies of β''-alumina electrolytes sealed to α-alumina insulating headers; (3) the shakedown and optimization of pilot plant unit operations for the production of β''-alumina electrolyte assemblies; (4) the development of improved seals between α- and β''-alumina; (5) the development of automated and/or non-destructive quality control test methods for electrolytes and sealed assemblies; (6) the development of, and delivery of, metal-clad rutile current collectors and/or containers. As part of the process development, alternative methods for forming and sintering β''-alumina tubes are being evaluated to support economic projection of ultimate electrolyte costs.

Significant progress has been made on optimizing the operation of the calcining furnace, ball mill, spray dryer, and batch (horizontal) sintering furnace. The processing of Meller and Reynolds (α-alumina) based powders has been optimized in the calciner and the ball mill while the optimization of slurry and slurry-solution spray drying was accomplished on powders derived from Bayer process α-aluminas (Reynolds and Alcoa).

Recent processing developments include: (1) exploratory, but very encouraging results on several inexpensive (<\$2/kg) raw material sources of α-alumina; (2) the spray drying (slurry and slurry-solution) of Reynolds and Alcoa-based α-alumina powders at the pilot scale; (3) the preparation of flowable and pressable powders for isostatic pressing by a method other than spray drying; (4) progress on the development of an electrolyte fabrication process which eliminates the calcination and milling operations.

Plans for the remainder of 1979 and 1980 include: (1) completion of shake down and optimization of the pilot plant unit operations for large-scale pilot production (~150 delivered units/day); (2) design, construction, and placing into operation a continuous sintering furnace capable of sintering up to 18 electrolytes (33 mm o.d. × 250 mm long) per hour; (3) specifying materials and procedures for large scale pilot production of β''-alumina electrolyte assemblies; (4) establishing the feasibility of fabricating large β''-alumina electrolytes up to 50 mm in diameter and 600 mm in length; (5) establishing the technical feasibility of using metal-clad rutile current collectors and/or containers in sodium–sulfur cells.

Major technical problems which require resolution include: (1) the use of low-cost raw materials, powder preparation procedures, and sintering techniques for the production of β''-alumina electrolytes with acceptable dimensions, out-of-cell properties, and in-cell performance; (2) the development of reliable methods and inexpensive materials for sealing electrolytes; (3) the development of non-destructive testing techniques in quality control; (4) establishing the feasibility of rutile as a viable material for the cathodic current collector in a sodium–sulfur cell.

Recent publications

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10 R. S. Gordon, G. R. Miller, T. D. Hadnagy, B. J. McEntire and J. R. Rasmussen, Ceramics in high performance batteries, *Proc. 4th CIMTEC (Int. Meeting Modern Ceram. Technol.-Energy and Ceram.) Saint Vincent, Italy, 28 May - 1 June, 1979.*

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12 B. J. McEntire, G. R. Miller and R. S. Gordon, Sintering of polycrystalline ionic conductors: β''-Al_2O_3 and NASICON, *Proc. Fifth Int. Conf. Sintering and Related Phenomena, Notre Dame, Indiana, June 18 - 20, 1979.*