PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Sodium-Sulphur Battery

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BATTERIES

The sodium–sulphur battery

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[Plate 1]

Energy futures of the industrialized nations are expected to rely increasingly on energy storage. Batteries provide a versatile form of storage, and new markets for batteries in electric vehicles and for bulk storage of electrical energy could exceed £10^9 globally by the turn of the century.

The sodium–sulphur battery is a favoured candidate for these applications because of its projected energy density, which is up to five times that available for conventional batteries, and also because of its potential for cost reduction. Sodium and sulphur and other constructional materials are cheap and readily available. The cell has a solid electrolyte, made by sintering alumina containing about 10% sodium oxide, and operates at temperatures between 300 and 400 °C, where the electrodes are liquid.

Development of the battery has now reached the engineering phase, and the technological challenges that are being addressed fall in the fields of reliability, cost and performance, battery design, safety, application engineering and production engineering.

INTRODUCTION

The idea of the sodium–sulphur battery using a solid ceramic electrolyte was conceived in the early 1960s by J. Kummer and N. Weber working at the Scientific Laboratories of the Ford Motor Company at Dearborn, Michigan, in the United States of America. At around about the same time a related concept in which glass fibres act as a solid electrolyte was concevied independently by Charles Levine of the Dow Chemical Company. Since that time significant development efforts have been set up around the world.

A major group, employing between 50 and 100 full-time staff, is based at the Ford Aerospace and Communications Corporation in California, where the original Ford work is continued. A major competitive effort has also been established at the General Electric Company in Schenectady. The U.S. programmes are targeted on the utility load levelling market where there is expected to be over \$$10^9$ business available by the turn of the century. A similar market for electric vehicle batteries is thought to be possible, but there is less emphasis on this in the U.S.A. at present. There is also an increasing interest in the possible use of batteries for storage of solar energy.

In continental Europe, a major development effort on sodium–sulphur batteries is centred at the German division of Brown Boveri based at Mannheim and Heidelberg. This is a very active programme, targeted on the electric car, which could be of strategic importance in Germany because of the absence of any national oil resource.

The effort in France is centred at the Marcoussis Laboratories of the C.G.E., which is partly funded by American subcontracts. Load levelling requirements in France are satisfied by

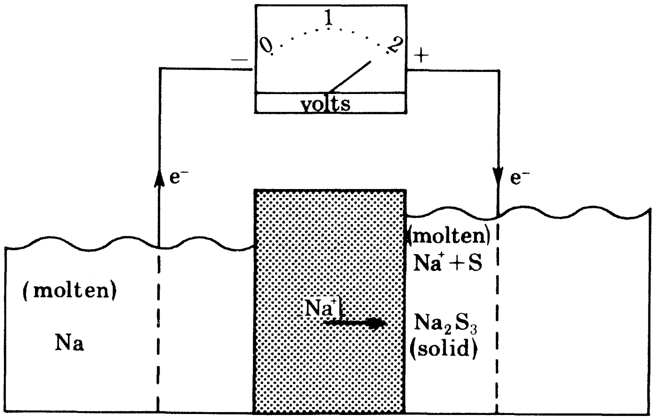


FIGURE 1. Principle of operation of the sodium–sulphur cell.

hydroelectric schemes, and vigorous support for electric vehicles may not be forthcoming from the French Government because they are not seen to provide significant energy savings over internal combustion vehicles, although they do provide significant savings of imported oil.

Work began in the United Kingdom at British Rail and the Electricity Industry Laboratories immediately after the Ford announcement in 1966 of the discovery of the sodium–sulphur cell, and somewhat later work began at Harwell. In 1974 the separate programmes were coordinated and a national programme was formed. Chloride Silent Power, jointly owned by Chloride and the Electricity Council and supported by the Department of Industry was formed at the time, ensuring the involvement of private industry and a mechanism for the commercialization of the technology in the U.K. The work in the U.K. is aimed at road and rail vehicle applications. This paper relies heavily on contributions from British Rail and Harwell, although most of the illustrations relate to the work at Chloride Silent Power.

The principle of operation of the device relies on two liquid electrodes separated by the solid electrolyte membrane, which is completely impermeable to sodium metal and sulphur but is permeable to sodium ions. However, when an external circuit is completed, sodium ions are able to diffuse through the solid electrolyte and the electrons pass round the external circuit into the sulphur electrode. The sulphur electrode is impregnated with carbon fibres, which produce electronic conductivity and also provide sites for the electrode reactions at which the discharge product, sodium polysulphide, is formed.

SOLID ELECTROLYTE MATERIALS

Although some new candidate materials have been discovered recently, the preferred electrolyte is a ceramic sodium aluminate formed by conventional ceramic methods and fired either by a rapid pass-through firing method pioneered by the Electricity Council Research Centre or by programmed batch firing methods developed at the British Rail Technical Centre. The development of the ceramic has now reached the stage where the material can be regarded as an engineering ceramic material, illustrated by the fact that it can be processed by automatic cutting and grinding equipment.

Examination of the structure by optical microscopy shows that recrystallization can be controlled to provide interlocking grains of around 100 μm in diameter. However, the fast firing technique can also be modified to yield a superfine microstructure, which provides great

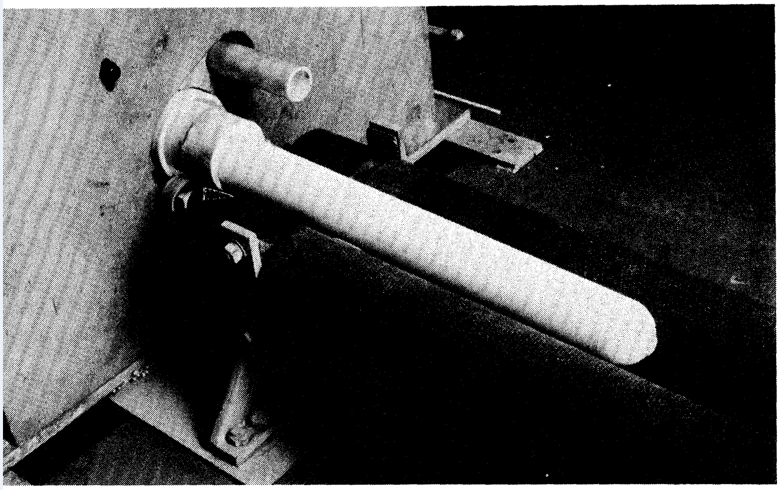


FIGURE 2. Production of β-alumina ceramic by zone sintering.

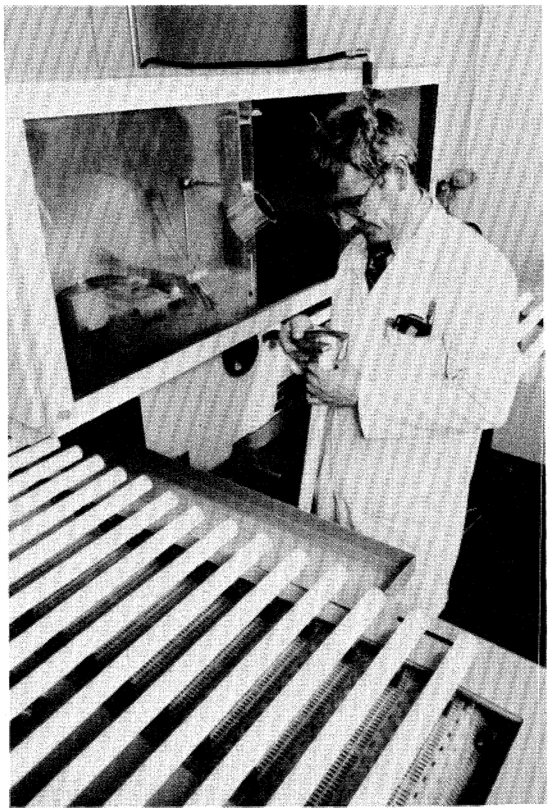
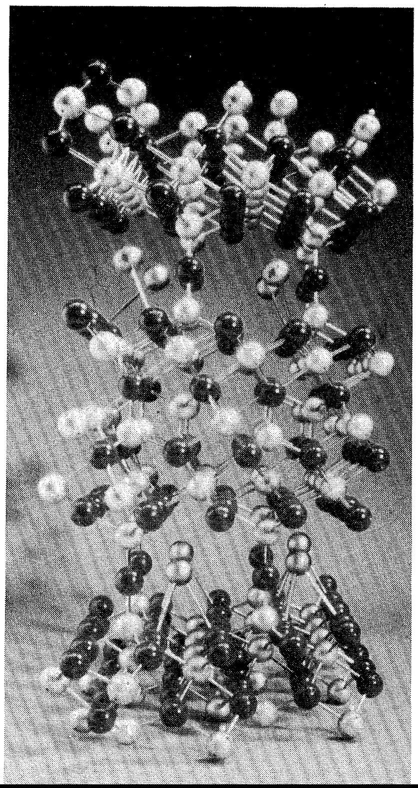


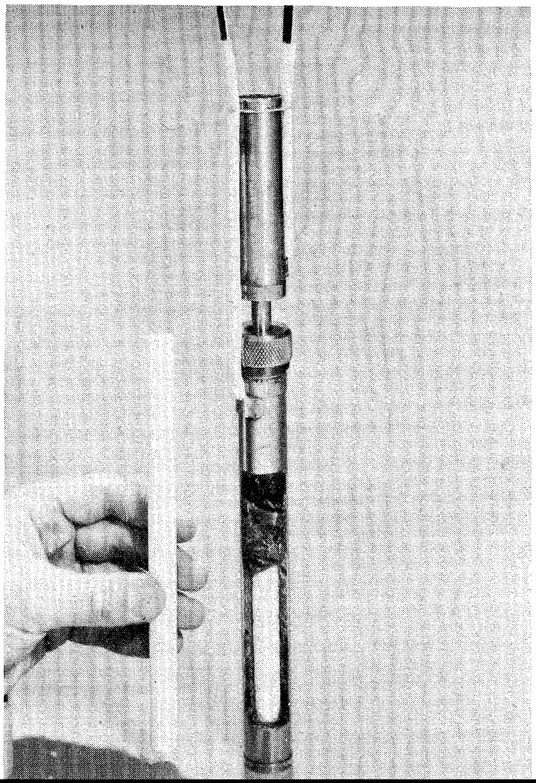
FIGURE 3. Semi-automatic cutting and grinding of ceramic electrolyte.

mechanical strength in ceramic materials. Generally, the finer microstructures make the ceramic electrolyte more resistive and current development programmes are seeking to understand and develop optimum structures for performance and durability.

Within the crystal structure of β-alumina, planar conduction channels are separated by four layers of close-packed oxygen ions. There are two crystallographic variants of β-alumina, β and β″. The latter, stabilized by addition of magnesium or lithium doping, is the more conductive but is also more difficult to process. Again, current development programmes are seeking to develop optimum doping levels for performance and durability.

At the present stage of development, ceramic lives in excess of 1000 cycles can be obtained. One model links failure to the propagation of long narrow cracks that exist at the sodium electrode surface of the ceramic owing to the Poiseuille pressure caused by the flow of sodium in the cracks. Theoretical analysis of the model indicates that insufficient pressures to cause propagation can be maintained unless the current density is increased by more than an order of magnitude from the practical values. More recent models seek to explain failure by the presence of current concentration in the bulk and at the surface. The surface of the solid electrolyte is therefore an important field of study in connection with the further development of the durability of ceramic electrolyte.





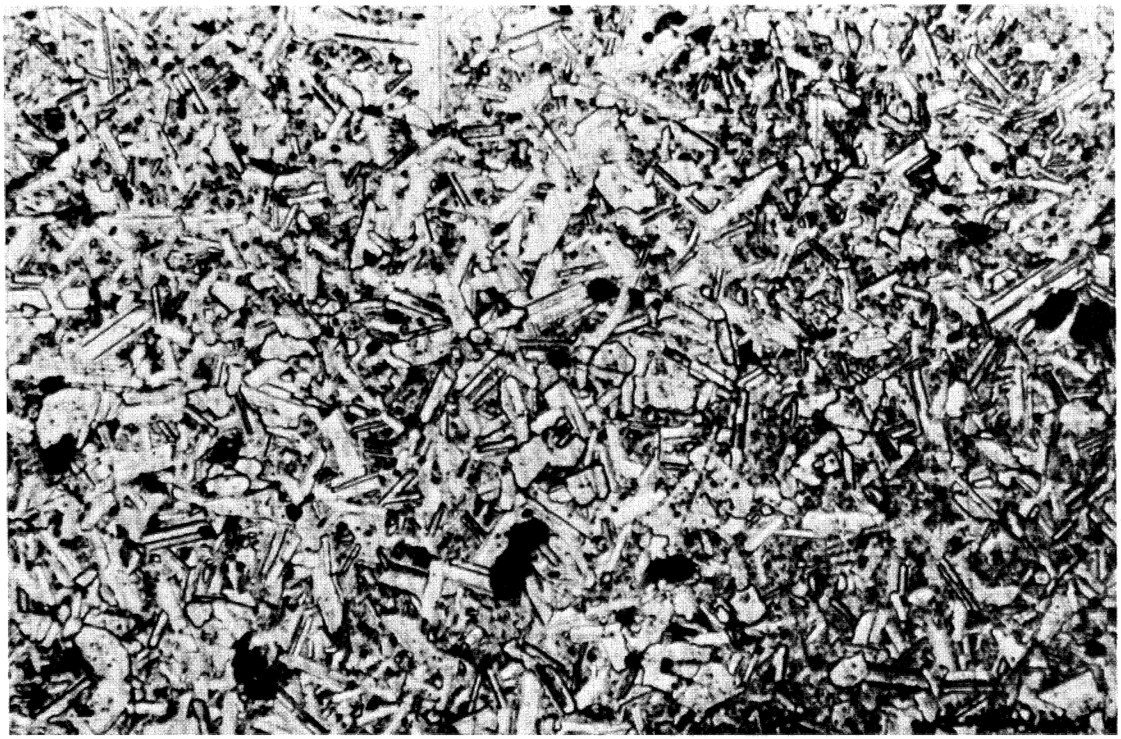


Figure 4. Ceramic microstructure demonstrating a controlled amount of recrystallization. (Magn. × 185.)

Figure 5. Superfine solid electrolyte microstructure produced by zone sintering.

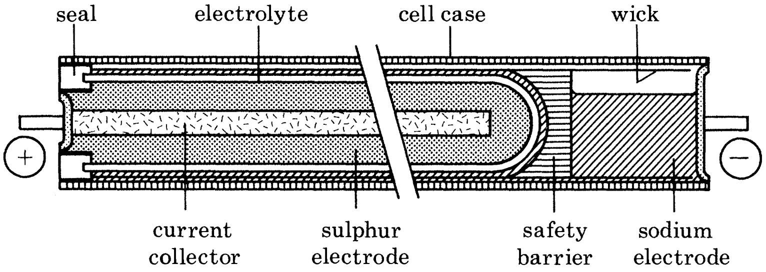


FIGURE 8. Schematic design of a central sulphur cell operating horizontally.

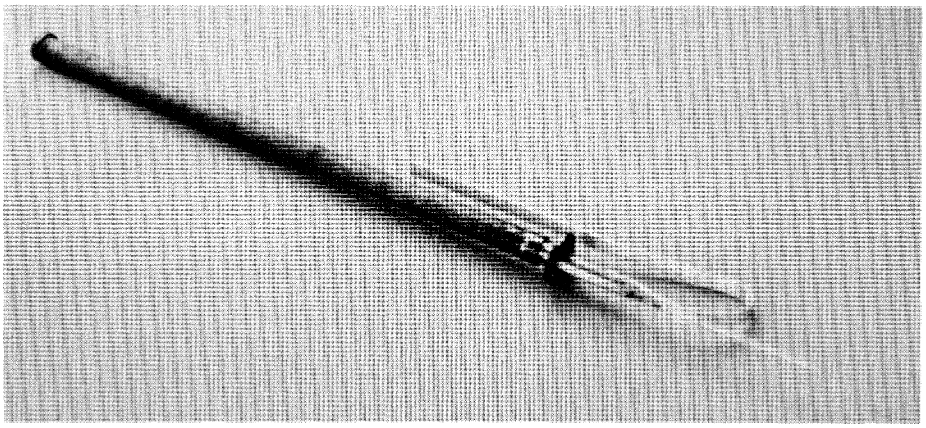


FIGURE 9. Rod current collector for the central sulphur design.

ELECTRODE DEVELOPMENT

The central sulphur design readily lends itself to providing a gravity feed for sodium by being operated seal downwards. Alternatively, workers at British Rail have shown that the cell can be operated vertically with the seal at the top if the sodium is fed siphonically from a pressurized capsule underneath the cell. In circumstances where it is convenient or necessary because of restricted space to operate the cells horizontally, it has been found that capillary feeders are able to supply sodium at a rate sufficient for rapid discharge of cells. The sodium electrode interface with the solid electrolyte is an active research topic because recent work, notably that of Demott at the British Railways Technical Centre, has demonstrated that a problem of increasing cell resistance is located at the sodium–electrolyte interface. This interface is also considered to provide the origin of ceramic degradation by crack propagation.

One of the major advantages of the central sulphur design is the transfer of the problem of corrosion from the inside of the container to the outside surface of a central rod. Pure graphite was a suitable current collector for the experimental cells in which the first experiments on the design were carried out. However, graphite was not sufficiently conductive for use in commercial cells, particularly cells for motive power applications where discharge capabilities of less than the 2 h rate are sometimes specified. Therefore, composite current collectors with an aluminium core and a conductive corrosion-resistant exterior have been developed. The most suitable materials for the exterior are carbon and certain semi-conductive oxides such as niobium doped rutile, which are inert in the sulphur electrode. Aluminium is not suitable for use without external protection because the normal corrosion products are insulators and cause passivation

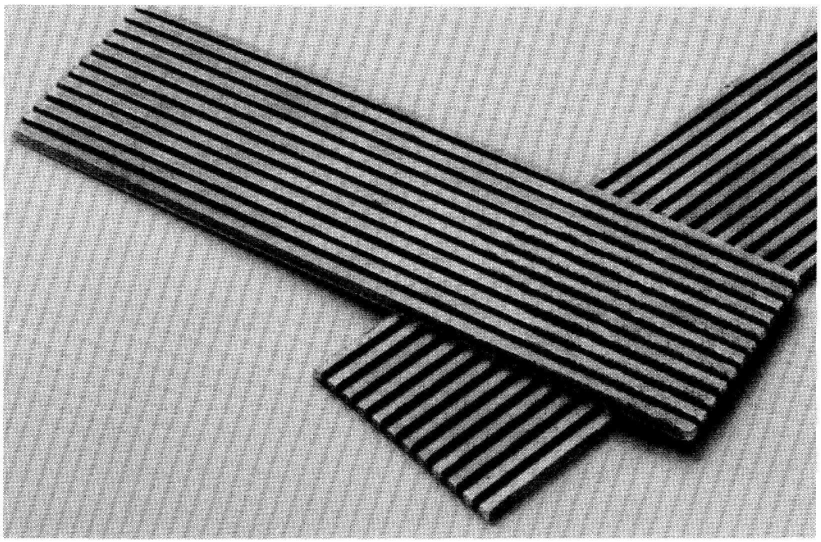


FIGURE 10. Multi-segmented sulphur electrode preform.

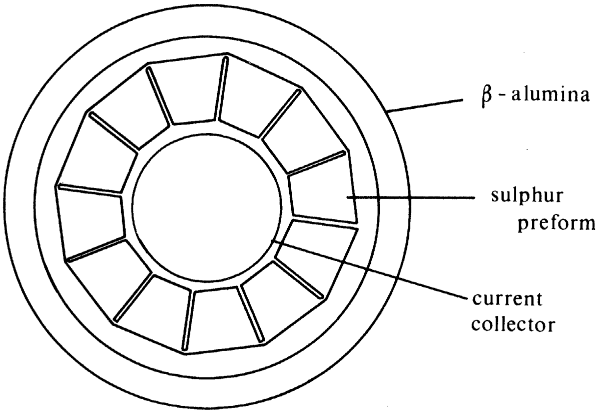


FIGURE 11. Schematic diagram showing arrangement of multi-segmented preform in cell.

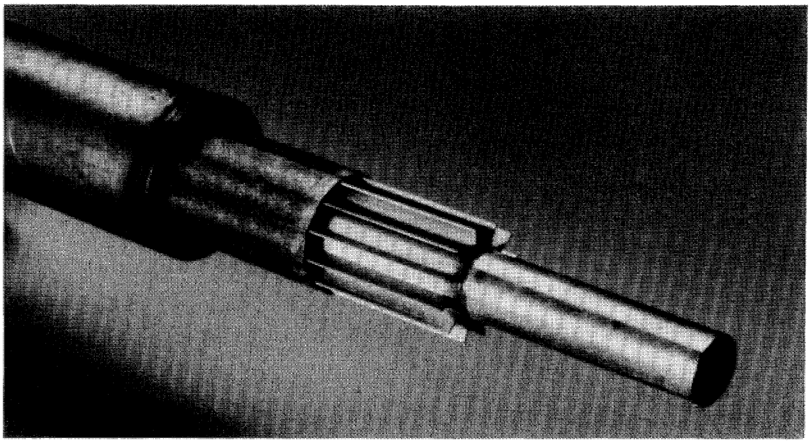


FIGURE 12. The use of a finned current collector in conjunction with a segmented electrode.

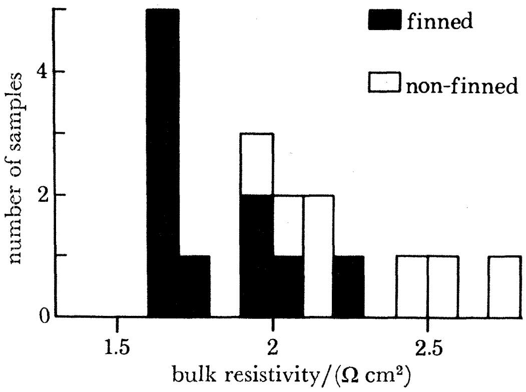


FIGURE 13. Reduction in electrode resistance arising from the use of a finned current collector.

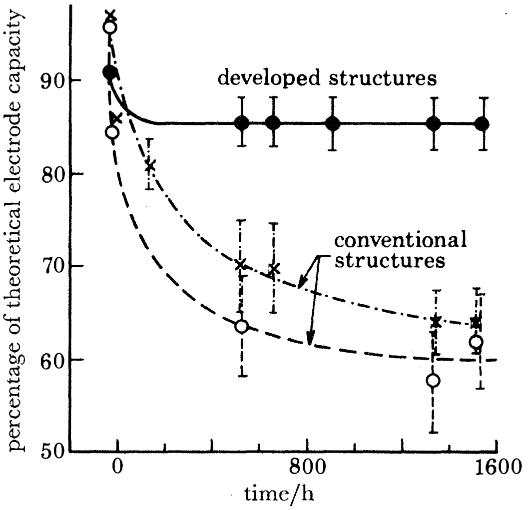


FIGURE 14. Illustration of improved capacity retention available from sulphur electrodes with modified capillary properties.

TABLE 1. INFLUENCE OF WETTING PROPERTIES ON SULPHUR ELECTRODE OPERATION

carbon fibres are:
(*a*) well wetted by sulphur
(*b*) less well wetted by polysulphide

alumina fibres are:
(*a*) well wetted by polysulphide
(*b*) not well wetted by sulphur

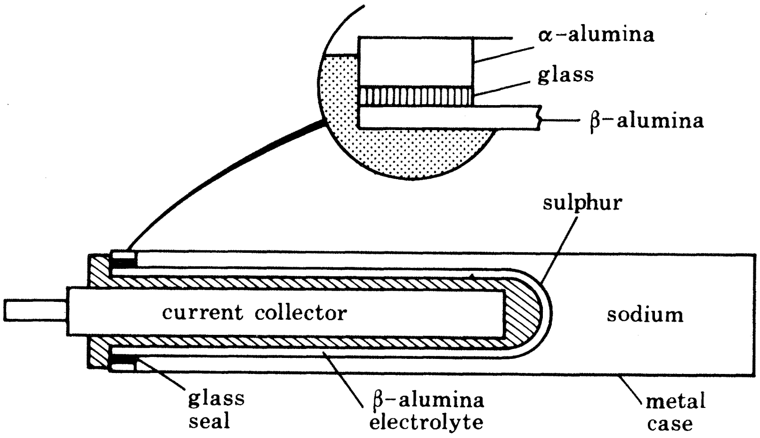


FIGURE 15. The use of glass–ceramic seals in the sodium sulphur cell.

of the electrode. Many useful constructions of aluminium-cored current collectors are proprietary at present and details of their construction have not been published.

The sulphur electrode contains carbon fibres under compression in the electrode annulus. Electrode-forming methods have been developed to premould a compressed shape outside the cell in a suitable form to fit inside the annulus. A multi-segmented form is a useful structure that

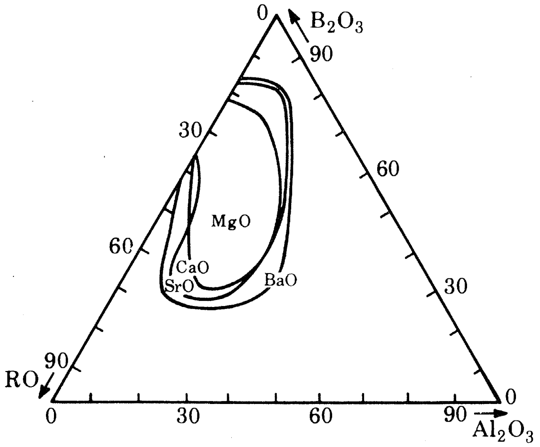


FIGURE 16. Aluminoborate glass-forming regions; R = alkaline earth.

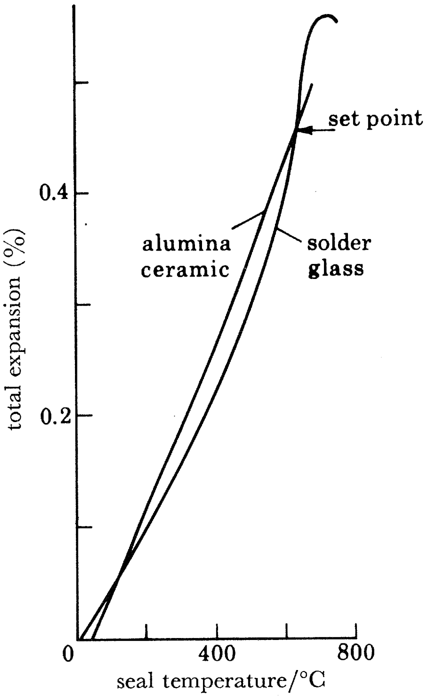


FIGURE 17. Relative expansion of aluminoborate glasses and alumina ceramics.

has been produced by development of commercial moulding methods to the pilot plant scale of manufacture. This shape is convenient for use with a finned current collector construction, which causes significant reductions in electrode resistance.

Another problem of the sulphur electrode that has been solved is the retention of capacity; 100% of theoretical capacity is defined to be the ability of the electrode to discharge to a composition corresponding to the trisulphide during discharge followed by complete recharge to sulphur during each cycle. Such performance is always obtained for the first few cycles with fibrous electrodes. However, with conventional electrode structures the usable capacity declines to around 60% of theoretical capacity. This has been found to be due to mass transport difficulties. Pockets of polysulphide become isolated from the electrolyte by regions of pure sulphur so that transport of sodium ions from the polysulphide is impeded, thereby preventing recharge.

Again, the problems of electrode operation have been solved by providing a means for transport of polysulphide from the remote regions of the electrode to the solid electrolyte. This is achieved by incorporating into the carbon felt, alumina fibres that are well wetted by sodium polysulphide. This composite electrode structure ensures that the two phases, sulphur and sodium polysulphide, exist as an intimate dispersion rather than as discrete regions of the two materials.

SEAL DEVELOPMENT

The solid electrolyte is sealed to the electrode compartment housings in two discrete stages. First the solid electrolyte is sealed to an inert ceramic insulator by using a proprietary glass. Sodium-resistant glasses with an appropriate expansion coefficient can be found among many combinations of alkali aluminoborates, many of which were developed for seals designed for

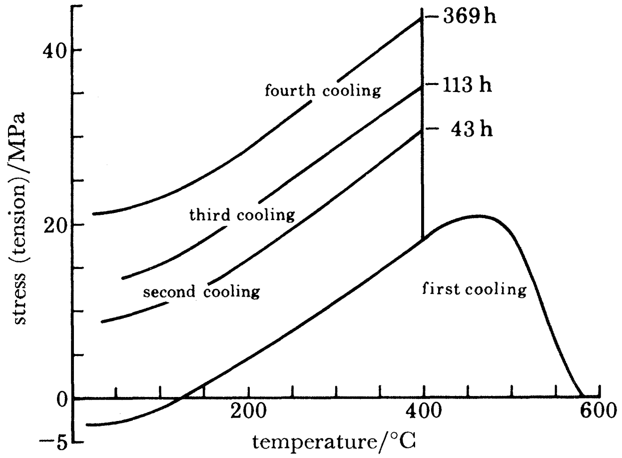
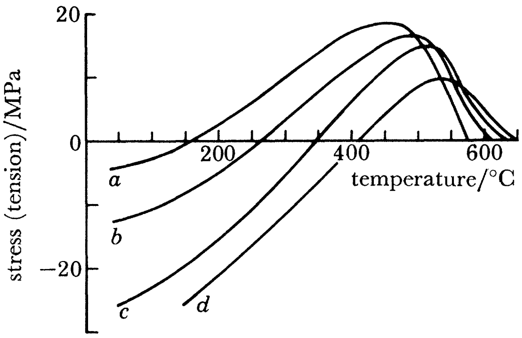


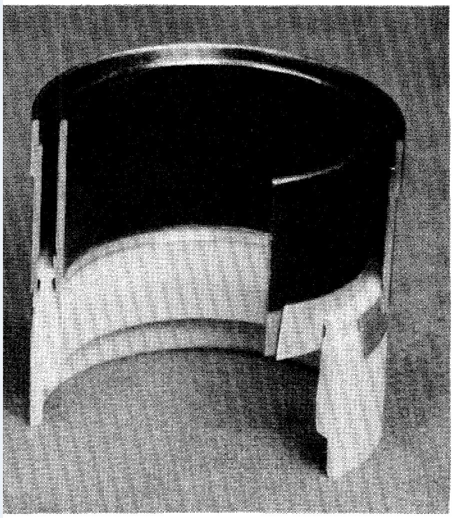
FIGURE 18. Stress development in glass seals at 400 °C resulting from densification processes. First heating was at 8 K/min; the rate of cooling was 6 K/min.



molecular percentage compositions.

	B_2O_3	Al_2O_3	BaO	SiO_2
a	55	24	21	0
b	47.5	23	21.6	7.9
c	43	22	20	15
d	33	23	21	23

FIGURE 19. Influence of silica additions on the stress characteristics of aluminoborate glass seals.



RE 20. Cut-away section of a radial diffusion bond seal for a sodium–sulphur cell.

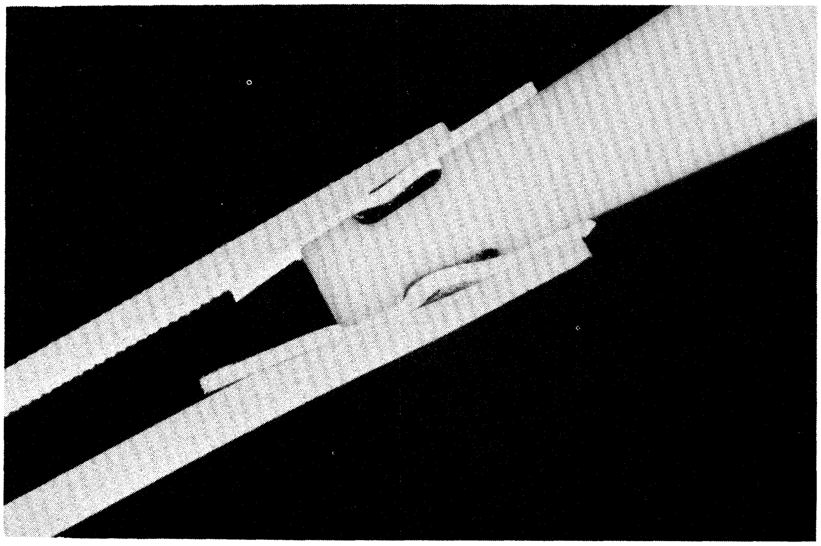
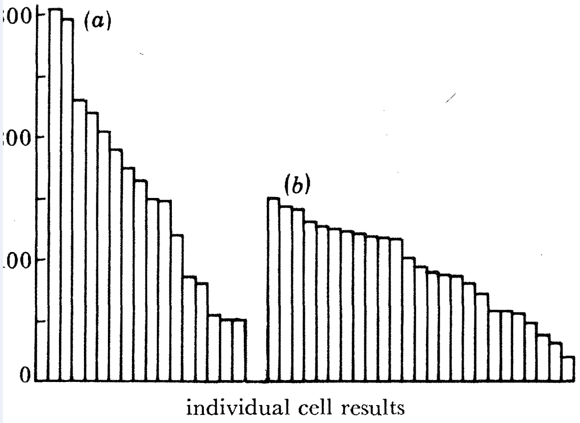


FIGURE 21. Micrograph illustrating deformation of aluminium that occurs during the bonding process.



URE 22. The use of safety features to improve cell safety. For ide cells (*a*), the mean temperature excursion was 158 K; ith improved safety features (*b*) it was 92 K.

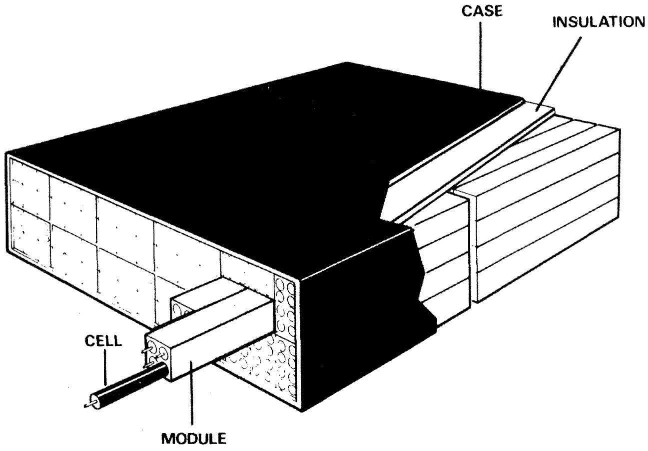


FIGURE 23. Modular design for a 480 cell battery.

operation at room temperature in a stress-free condition. As a consequence of the the nonlinear expansion coefficients of such glasses, seals between α- and β-alumina would normally be in tension at the operating temperature of a sodium–sulphur cell. Furthermore, such glasses have been shown to be dimensionally unstable at 350 °C as a result of molecular reorganization, which leads to densification and to the development of large tensile stresses in the sealed assembly. Considerable research has been carried out at Chloride Silent Power in association with the National Physical Laboratory to identify glasses that are to remain stable and stress free at the operating temperature of the cell.

The second stage of the sealing process involves ceramic–metal seals between the insulating collar and the electrode housings. The preferred solution to this problem now adopted worldwide is the thermocompression bond with the use of aluminium interlayers. Aluminium sealing rings are deformed under the combined effect of heat and pressure. The deformation process breaks up the protective oxide film on the aluminium and the substrate aluminium metal then bonds strongly to the metal and ceramic components. Pioneering work at Chloride Silent Power has led to a very compact seal arrangement that is contained within the cylindrical geometry of the cell.

SAFETY

A strong emphasis on safety development has been concerned with the containment of the vigorous reaction that can occur spontaneously in a sodium–sulphur cell if the electrolyte is fractured. This reaction is minimized in the central sulphur cell design because the sodium storage area is segregated from the sulphur electrode region. Nevertheless, there is sufficient sodium in the annulus for a vigorous reaction to occur. The severity of reaction can be judged from the maximum temperature recorded on the cell case after electrolyte fracture has occurred. It is necessary, because of the variable results of individual safety tests, to carry out many tests and subject the results to statistical analysis to predict event probabilities. Extreme value probability statistics are the most suitable and the technique has been applied for two cell designs. For the first design there is a 4% probability that a temperature excess of 300 °C, thought to be an

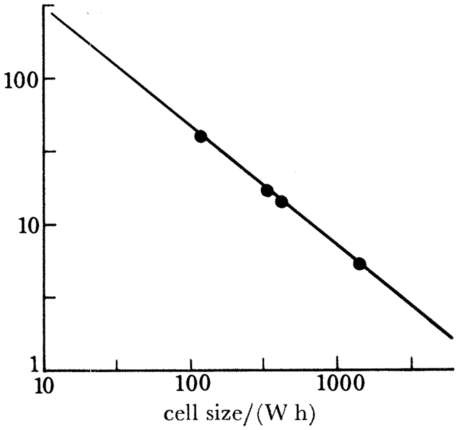


FIGURE 24. Economics of scale in cell manufacturing costs (excluding electrode materials).

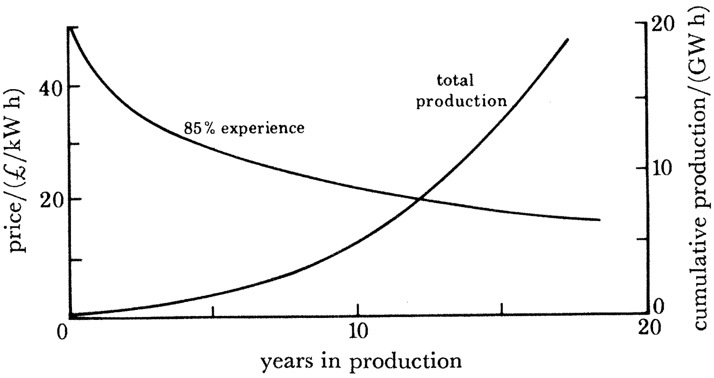


FIGURE 25. Experience curve projections for cost reductions during battery manufacture, assuming 20% growth annually.

acceptable target maximum, is exceeded. For the second design, which contains new safety features, a lower temperature excursion of 200 °C is predicted to occur with a frequency of 1 in 10^4 failures. There is confidence that a cell that is sufficiently safe can be produced.

COMMERCIALIZATION

The final stage of battery development concerns application engineering and the development of battery configurations and thermal management systems.

Some prototypes have been tested with varying degrees of success, but new and significant developments in modular insulated batteries are expected to be produced in the next year or so.

The other question that will control the general use of sodium–sulphur cells concerns manufacturing costs. Sodium, sulphur and carbon felt are all now cheap and readily available. Indeed they only contribute a few pounds sterling per kilowatt hour to the cost of the battery. There is a considerable amount of technology in the other components of the cell and in the encapsulation methods, which together dominate the manufacturing costs. However, there is now sufficient information available to support the belief that a first-generation sodium sulphur cell and the associated battery hardware will be cost-competitive with lead–acid batteries in the market place. These costs are not low enough to open up vast new markets for batteries, and it is necessary to consider how costs may be reduced. A first approach to this, which can be described as the microscopic approach, involves the reduction of the cost of individual components and manufacturing operations. A far more effective method of cost reduction, which can be referred to as the macroscopic approach, derives from a powerful economy of scale factor arising from increasing the size of a single cell. The commercialization of the sodium–sulphur battery should combine both microscopic and macroscopic economies, which will result in an experience curve that could halve battery prices in real terms within 6 years of the commencement of manufacture.

CONCLUSIONS

The development of the sodium–sulphur battery has now proceeded to the stage that there are good prospects that technical solutions are available for the remaining problems.

A significant problem concerns the need to improve the reliability of the solid electrolyte separator in the cell. This will be achieved by improvements to the solid electrolyte and its operating environment that will arise out of an increased understanding of failure mechanisms. There is considerable scope here for involvement of universities and other academic institutions.

There is a body of evidence that adequate safety of sodium–sulphur batteries can be achieved by development work aimed at appropriate segregation of the sodium and sulphur active materials. However, the commercialization of batteries for transport and energy storage applications will require significant innovations in thermal engineering.

The cost of sodium–sulphur batteries in commercial manufacture should be less than that of lead–acid batteries. The low cost will be achieved because of the low cost of materials, economies of scale in cell size, and cost reductions achieved from manufacturing experience.

I gratefully acknowledge the contributions of many colleagues at Chloride Silent Power whose work I have reviewed in this paper. I would mention in particular S. R. Tan, P. Blood, S. N. Heavens and G. Sands in connection with solid electrolyte properties and methods of manufacture; P. J. Bindin, S. Jackson, M. McNamee and S. MacLachlan in connection with seal development and cell battery engineering; R. O. Ansell, M. P. J. Brennan, D. J. Riley and M. Jagla in connection with the design of electrodes and their methods of manufacture; F. M. Stackpool for information on glass technology and safety; A. Gibson, B. Doeser and G. Woodier for test data; and G. R. Lomax and G. McGreavy for information relating to commercialization.

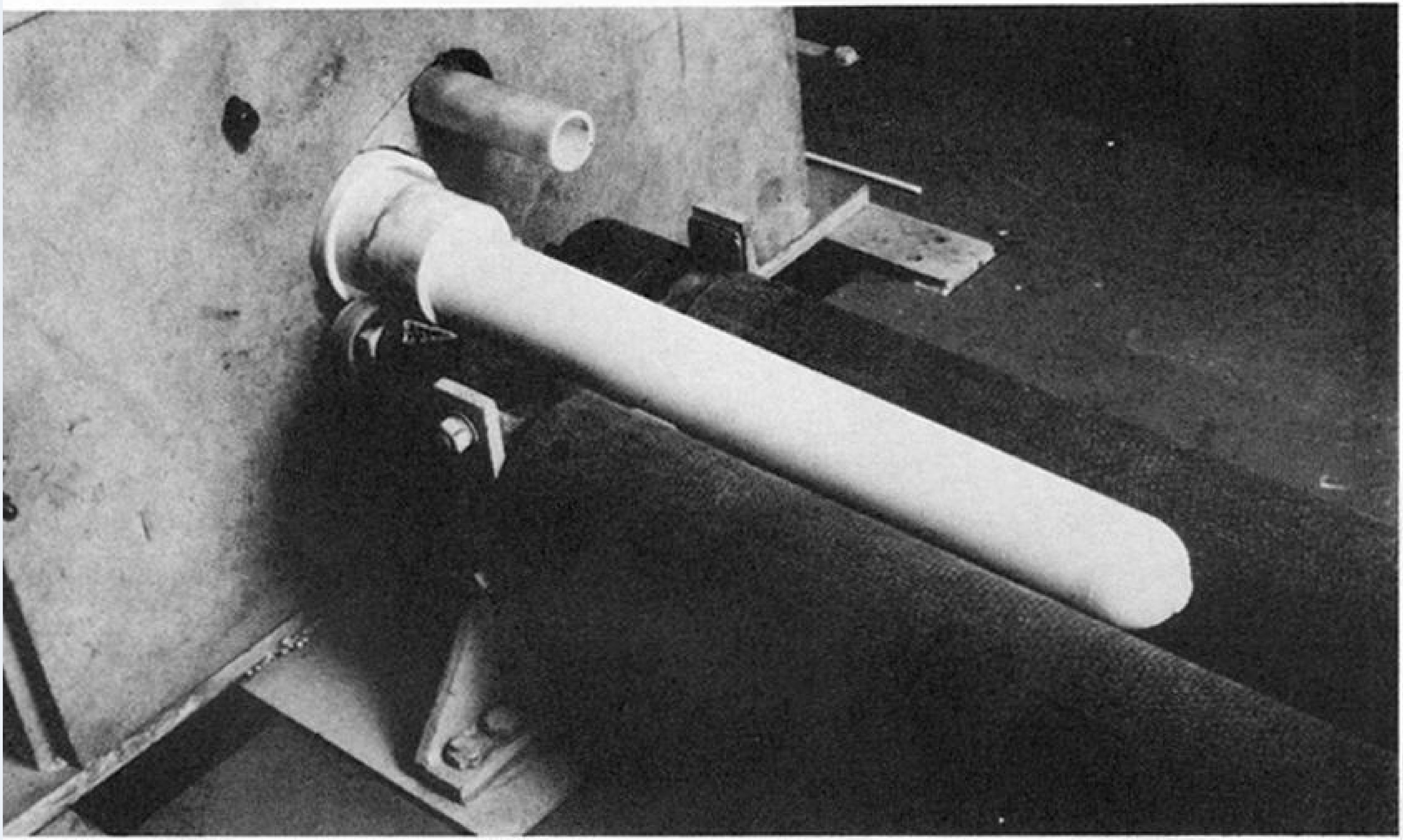


FIGURE 2. Production of β-alumina ceramic by zone sintering.

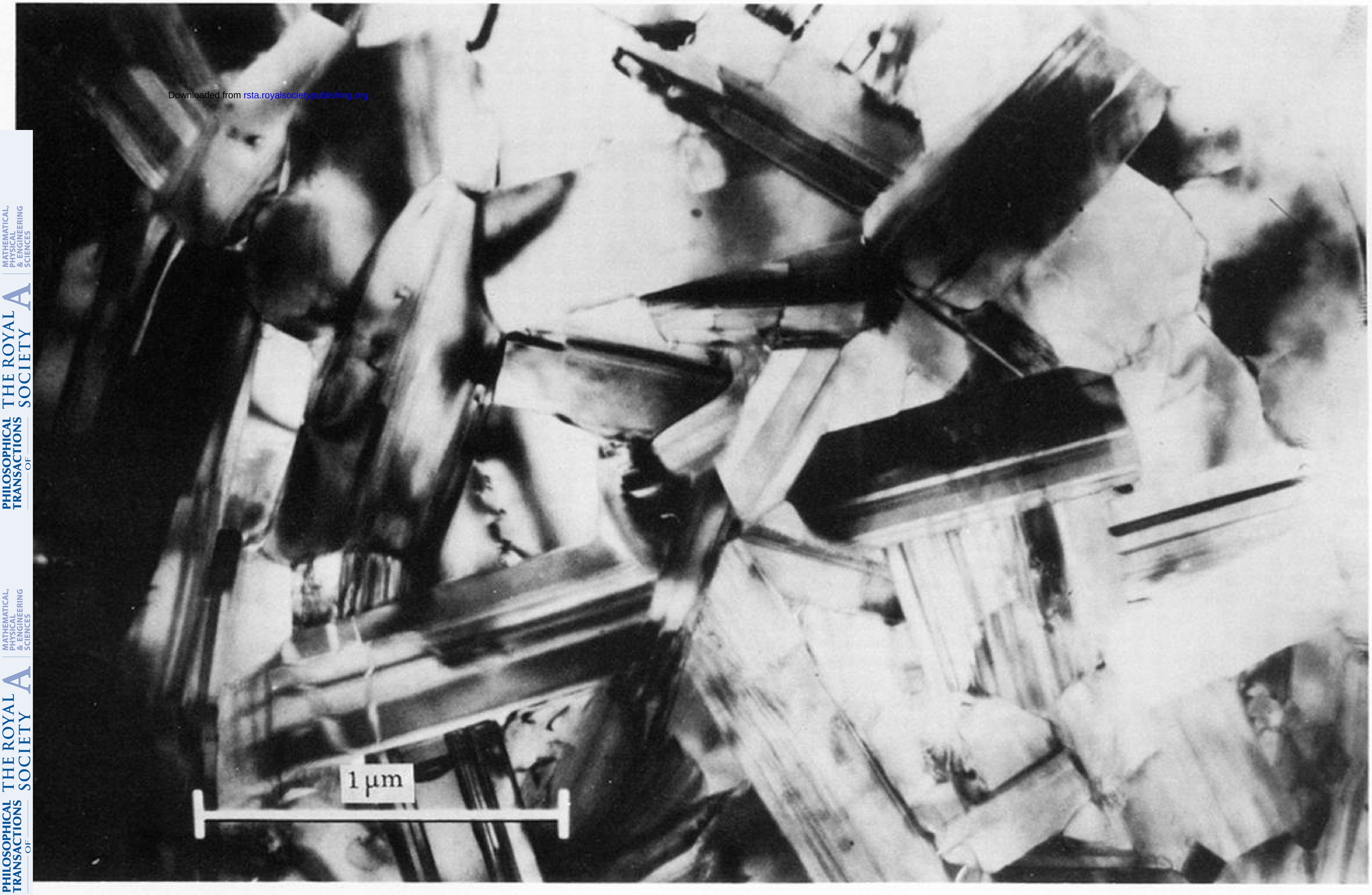
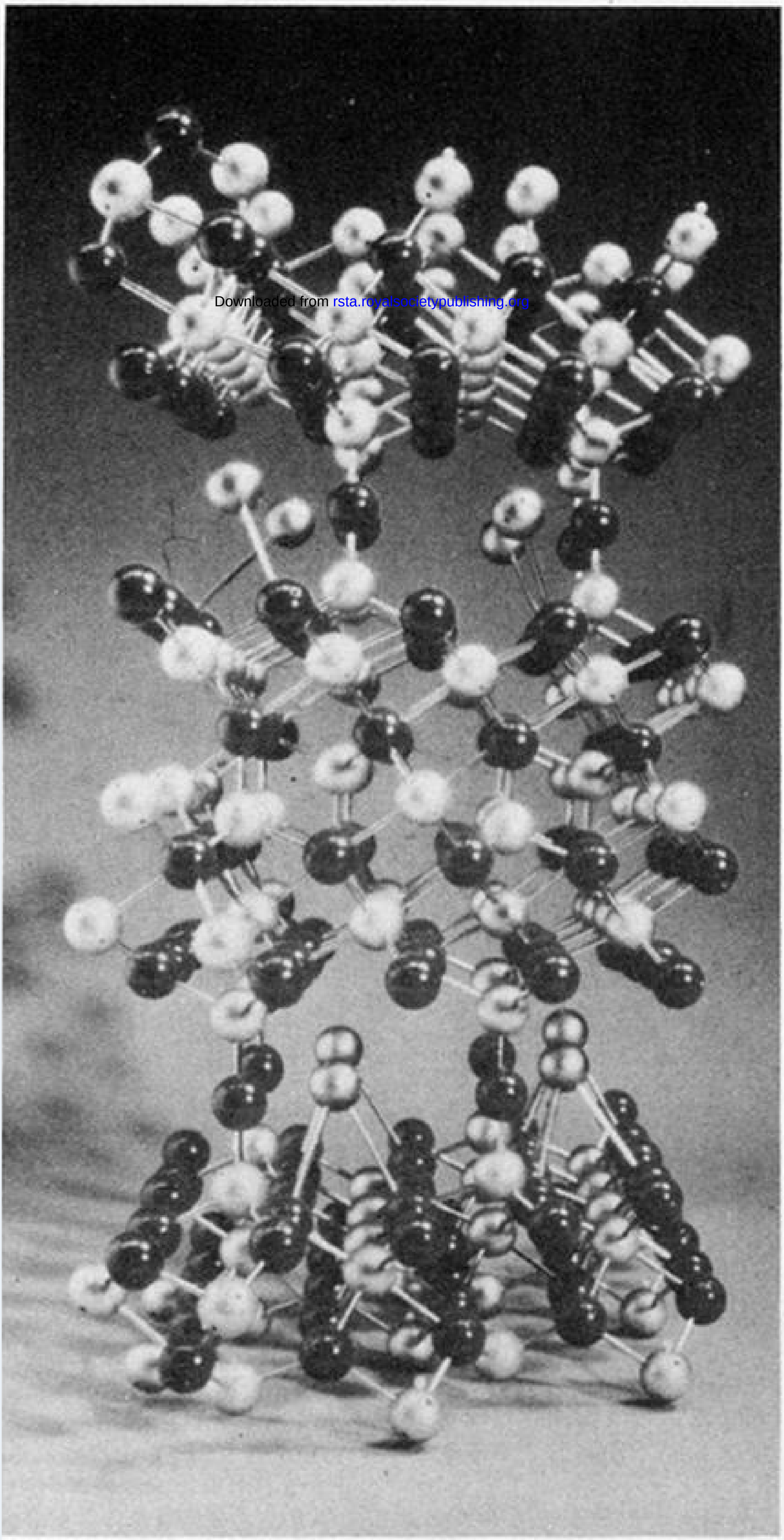
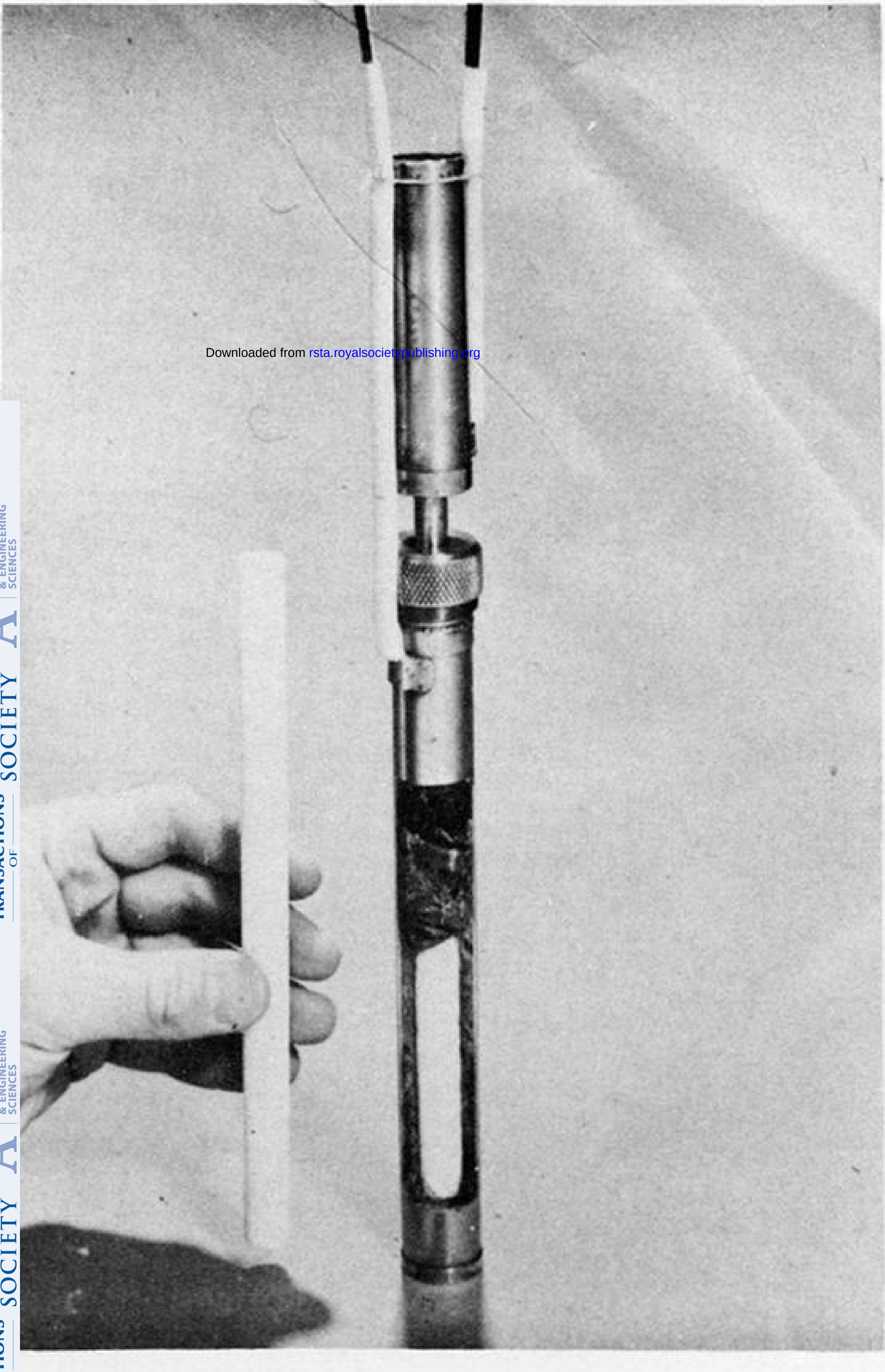


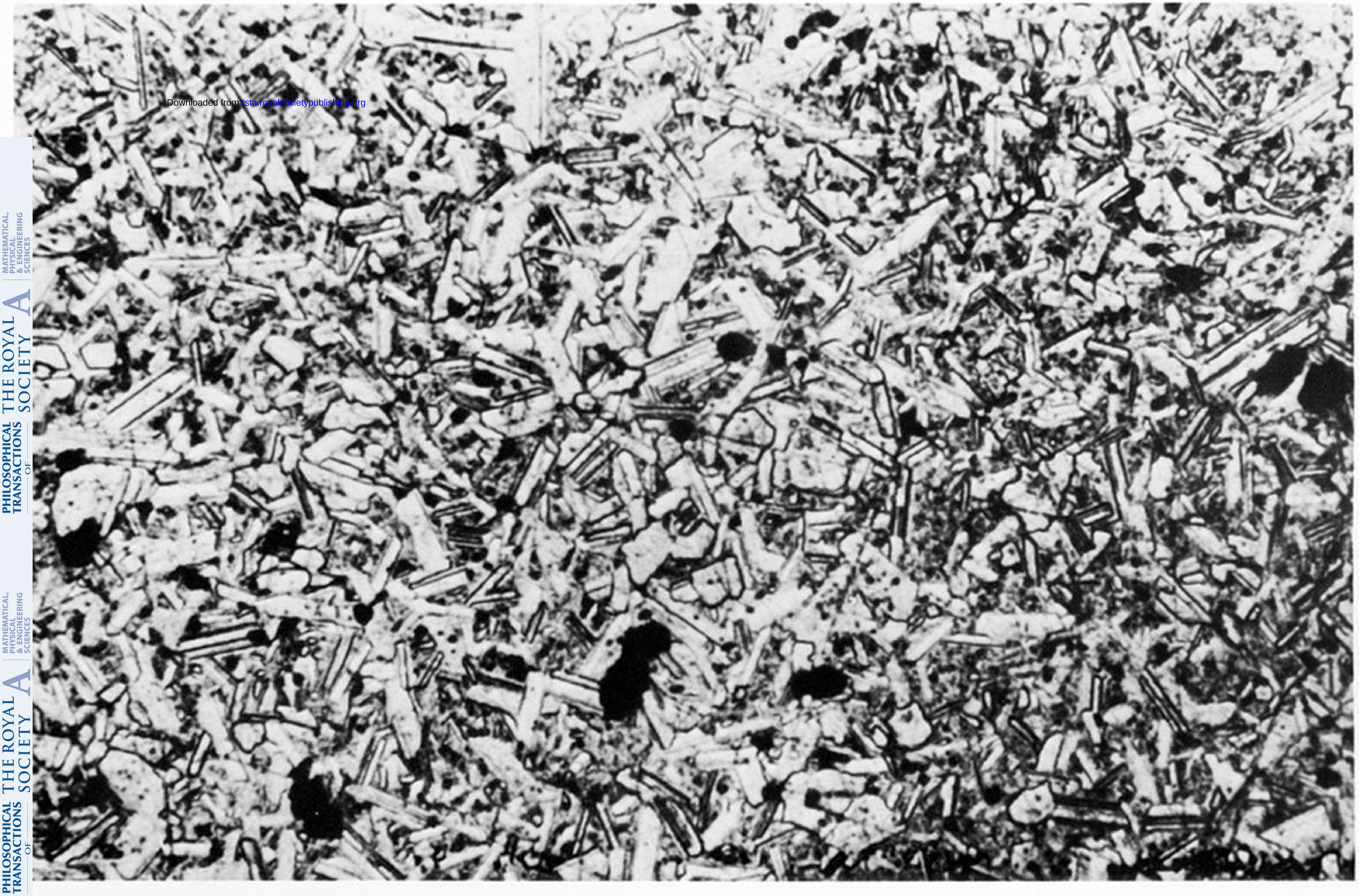
Figure 5. Superfine solid electrolyte microstructure produced by zone sintering.



IGURE 6. Model of β-alumina structure.



GURE 7. An experimental central sodium cell design with cell case cut away to show sulphur electrode construction.



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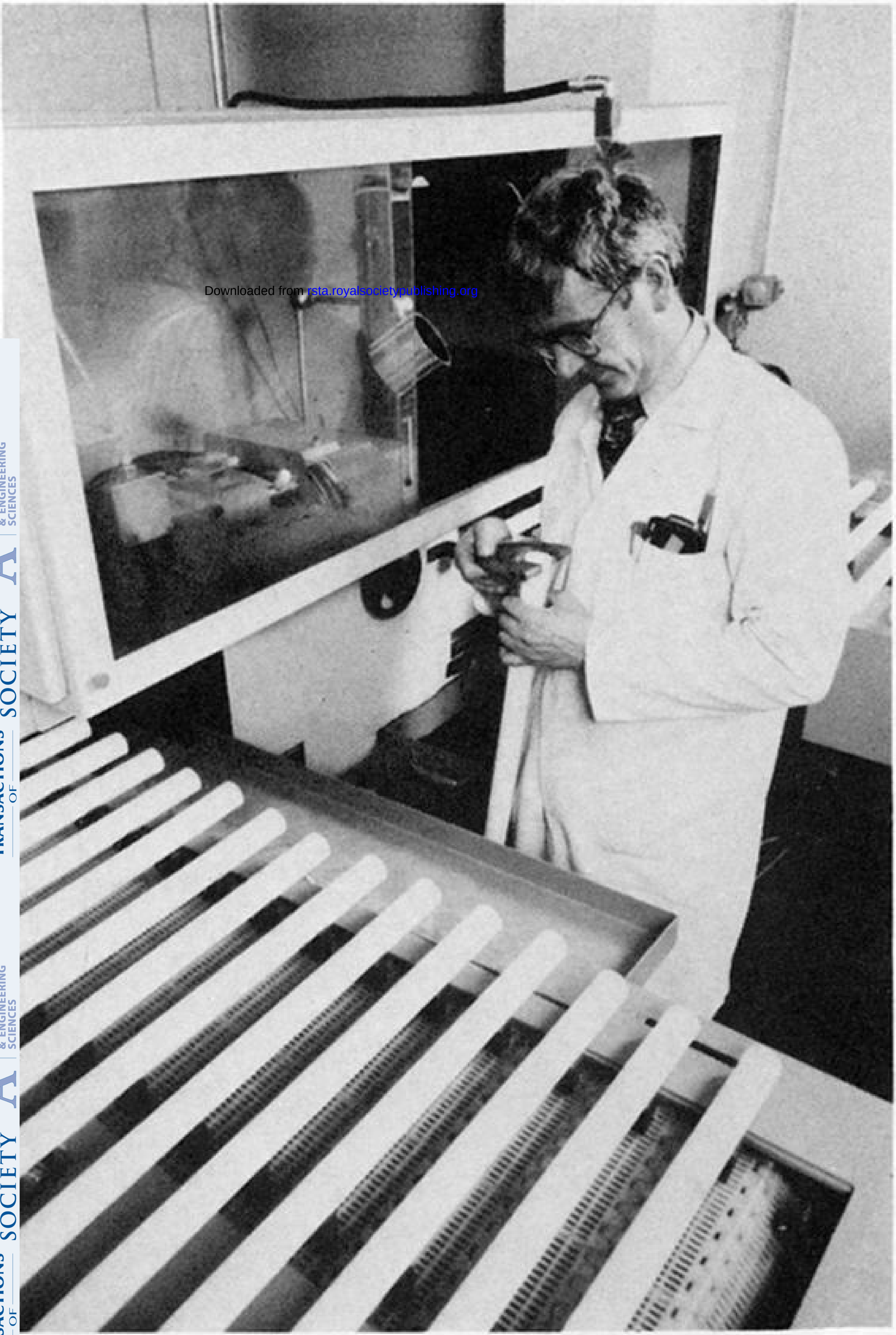

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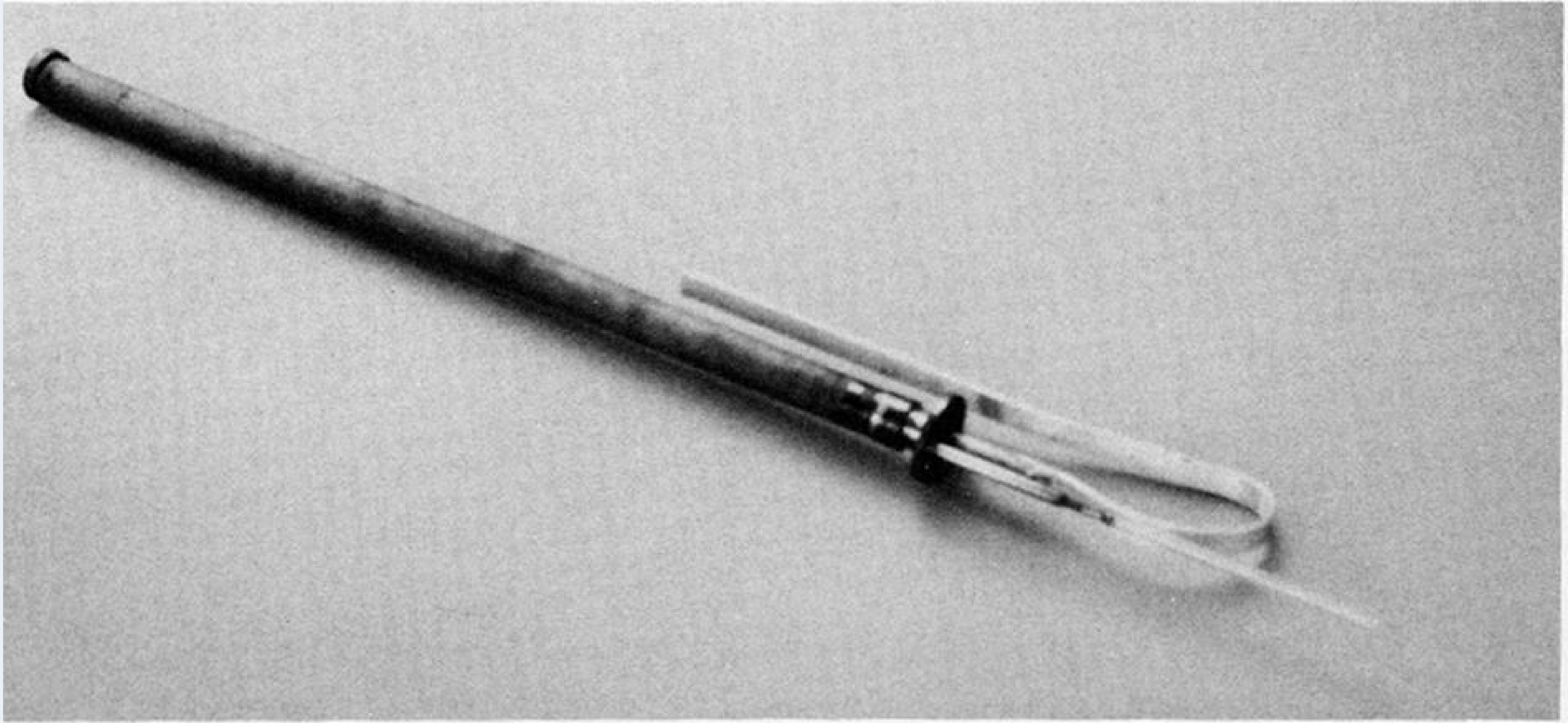

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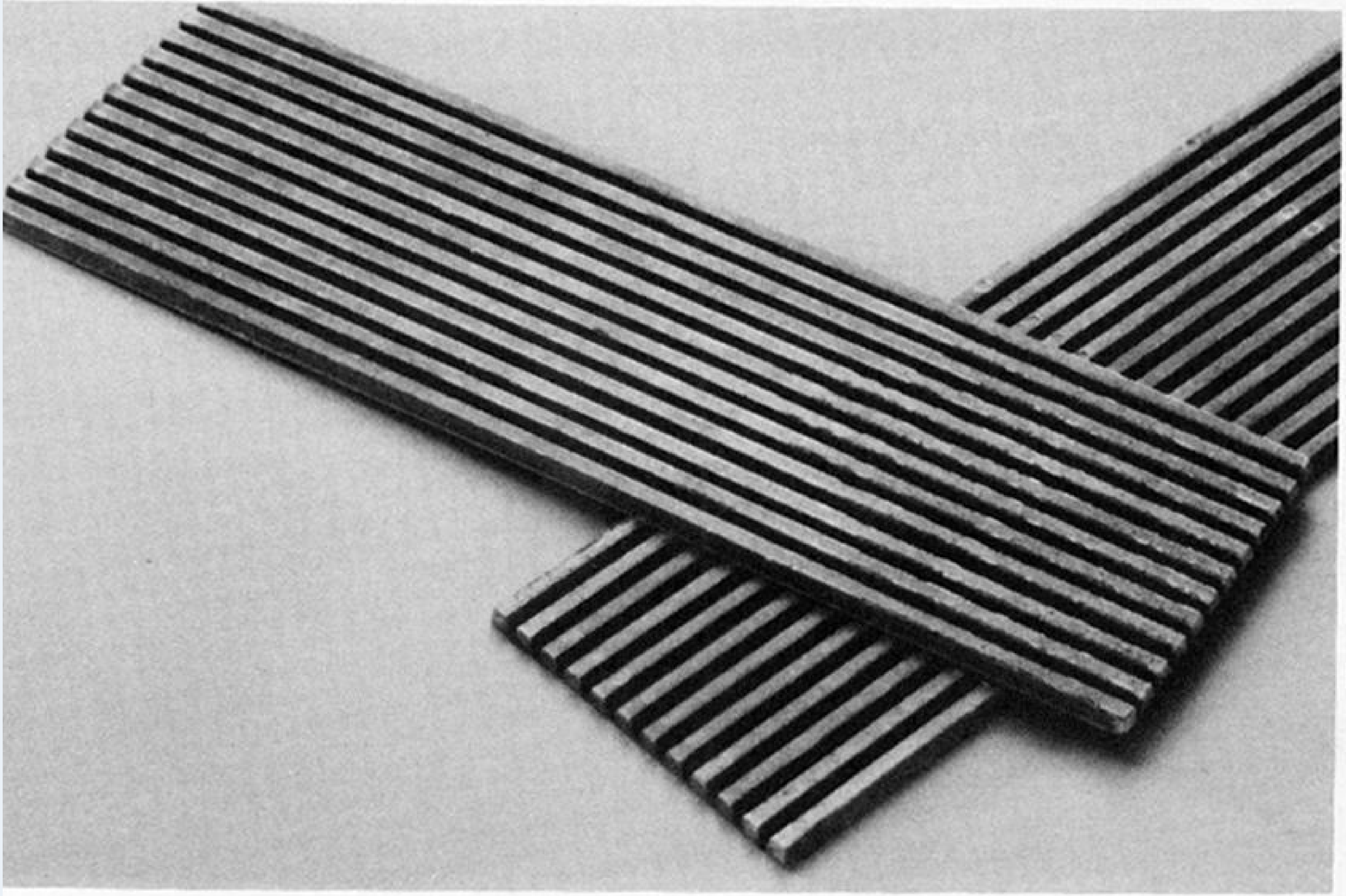


Figure 10. Multi-segmented sulphur electrode preform.

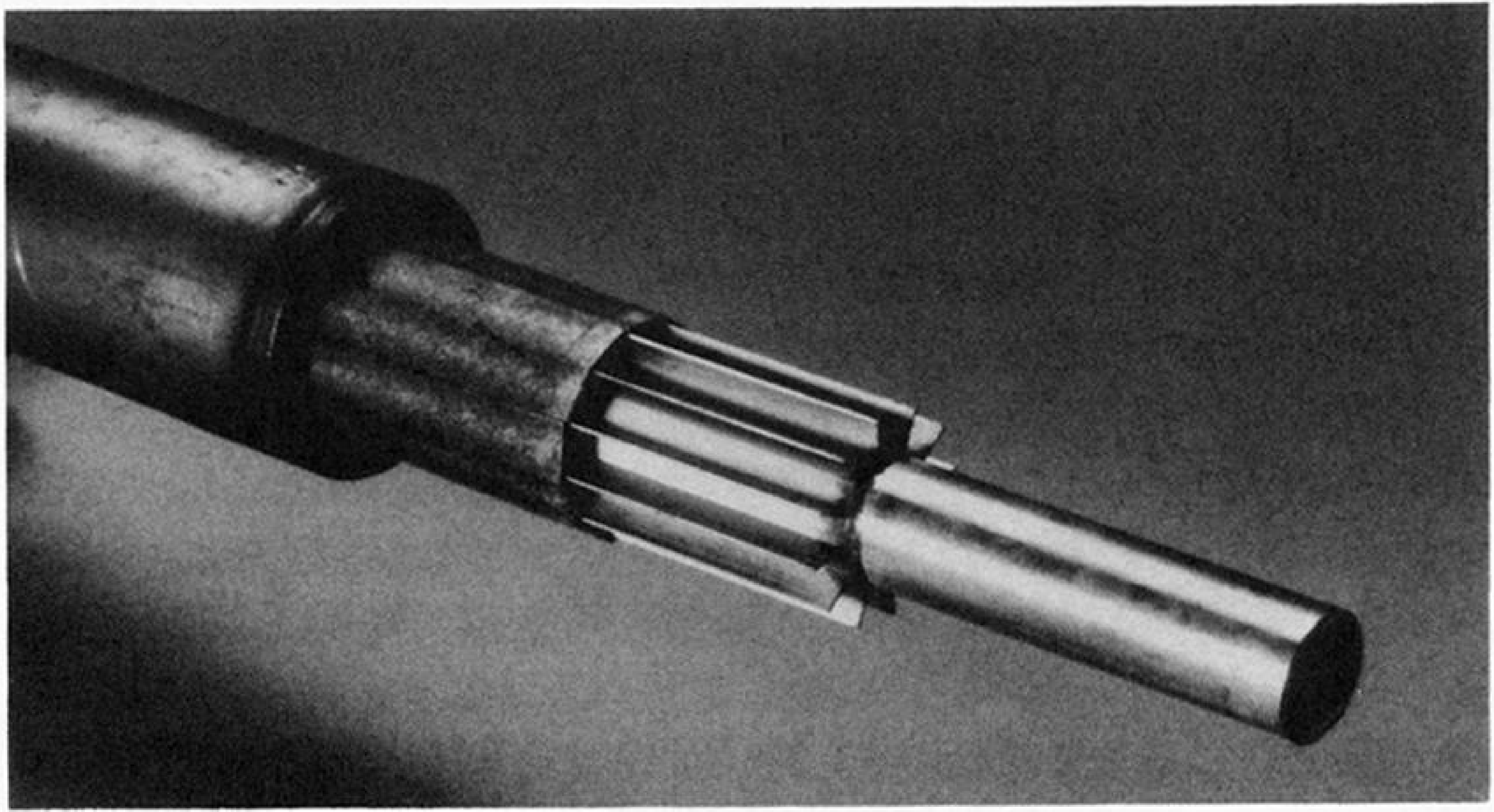
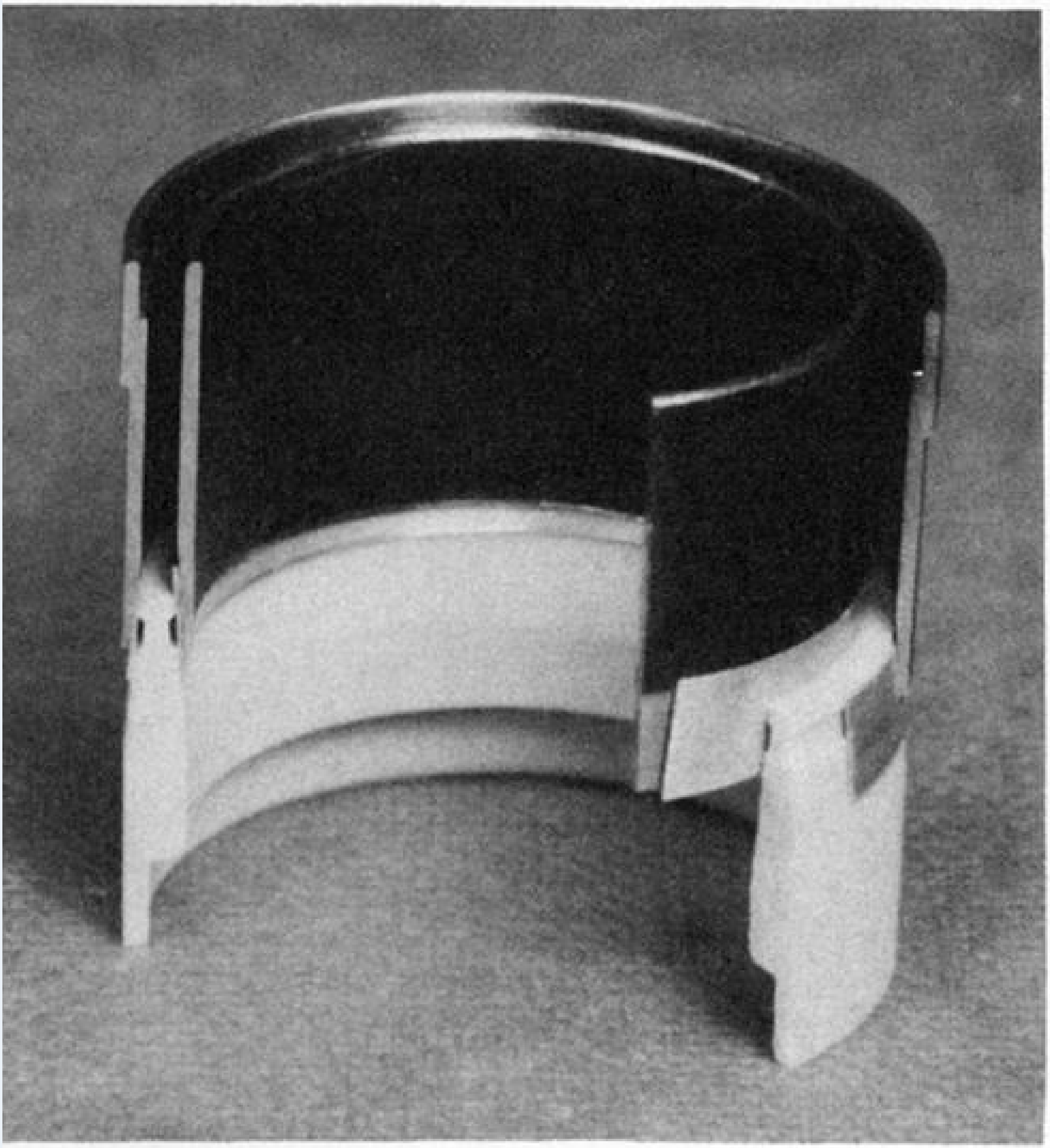


Figure 12. The use of a finned current collector in conjunction with a segmented electrode.



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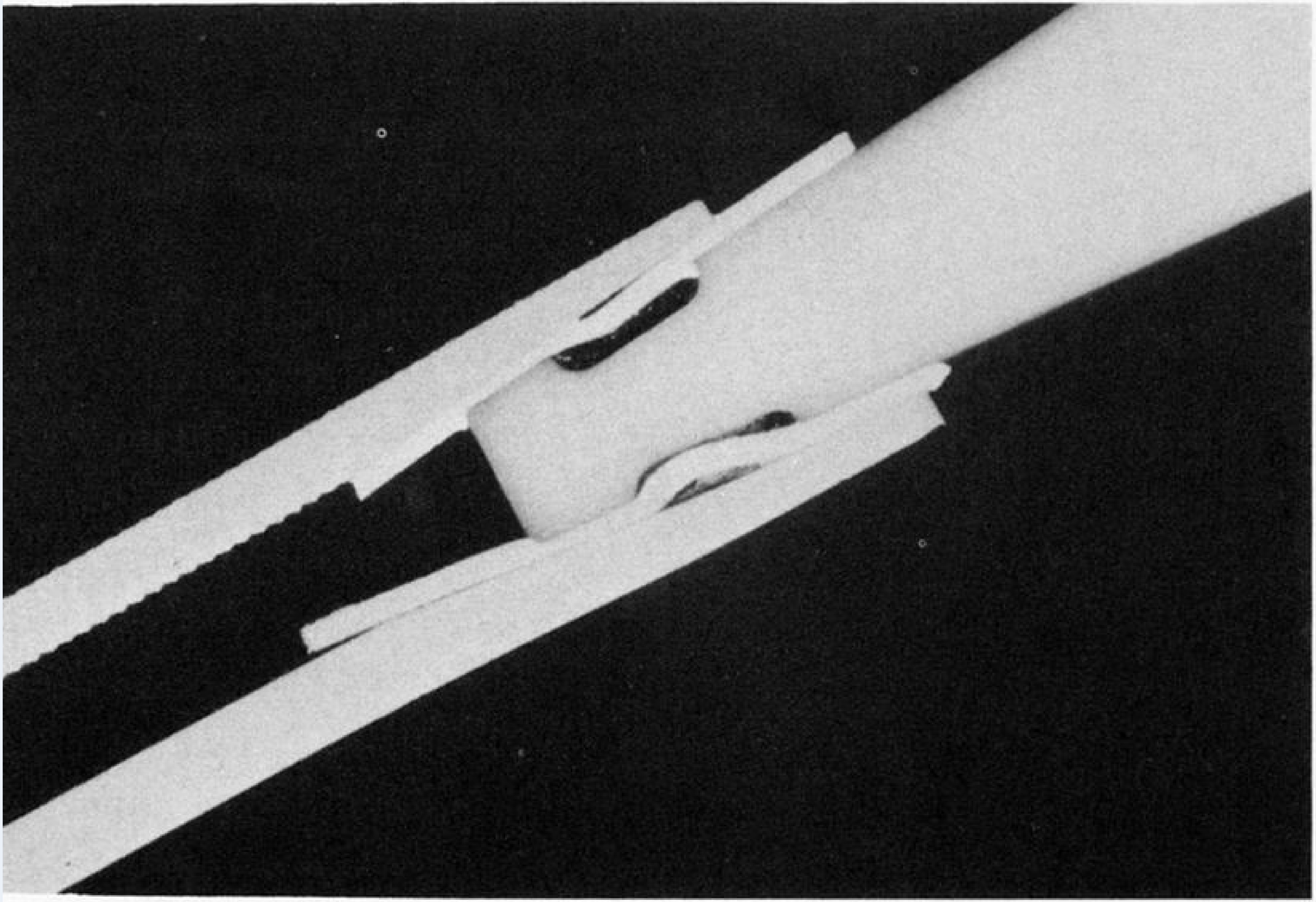
PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES



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