Research and Development in Non-Mechanical Electrical Power Sources

POWER SOURCES 10

RESEARCH AND DEVELOPMENT IN NON-MECHANICAL ELECTRICAL POWER SOURCES

Proceedings of the 14th International Power Sources
Symposium held at Brighton, September 1984

SPONSORED BY THE JOINT SERVICES
ELECTRICAL POWER SOURCES COMMITTEE

Edited by
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1985

THE PAUL PRESS LTD
22 BRUTON STREET
LONDON W1X 7DA

British Library Cataloguing in Publication Data

Power Sources.
Vol. 10
1. Direct energy conversion — Congresses
Pearce, L.J.
621.31'24 TK2896

ISBN 0-12-689160-5

Printed and bound in Great Britain by
Biddles Ltd, Guildford and King's Lynn

POWER SOURCES 10

Also in this series

BATTERIES. Research and Development in Non-Mechanical Electrical Power Sources. 1963

BATTERIES, 2. Research and Development in Non-Mechanical Electrical Power Sources. 1964

POWER SOURCES, 1966. Research and Development in Non-Mechanical Electrical Power Sources. 1967

POWER SOURCES, 1968. Research and Development in Non-Mechanical Electrical Power Sources. 1970

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POWER SOURCES, 8. Research and Development in Non-Mechanical Electrical Power Sources. 1981

POWER SOURCES, 9. Research and Development in Non-Mechanical Electrical Power Sources. 1983

FOREWORD

The 14th International Power Sources Symposium, held at Brighton from the 17th to the 20th September 1984, was attended by nearly 350 delegates from some 24 countries.

'POWER SOURCES 10' is an edited record of the proceedings of the symposium. It also includes a record of an informal discussion, held under the chairmanship of Richard Acton, dealing with storage batteries for "Renewable Energy Sources".

On a personal note, I am greatly indebted to my Committee colleagues and our professional officers for coping so well with the myriad of tasks associated with the Symposium including the publication of this book. Their helpfulness has been greatly appreciated.

Richard Acton and David West, who over many years have contributed so much towards ensuring that the Symposium achieves its goals, have recently retired from the Committee; they will certainly be missed for all the best reasons.

Finally I would like to thank all the authors and the associate editor for their helpfulness and co-operation in the preparation of these papers for publication.

Admiralty Research Establishment
Poole
November 1984

L.J.P.

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BATTERIES FOR RENEWABLE ENERGY SOURCES – AN INFORMAL DISCUSSION

D. Butterworth
R.G. Acton

The subject under discussion was the role of batteries in renewable energy systems. It was suggested that world reserves of fossil fuels are finite and that world demand will probably exceed supply by the middle of the 21st. century. Accordingly, it becomes vital that renewable energy sources are developed to fill the gap. The prognosis was deliberately pessimistic in order to promote discussion.

The renewable energy sources listed for consideration included Solar, Hydro, Tidal, Waves, Wind, Ocean Thermal Gradients and Plants. Nuclear Fission and Fusion were added to the list only after debate but limitation in time precluded any ensuing discussion. To provide further background some details of present energy consumptions in Western and Third World countries were also given i.e.,

U.S.A.	75,000 kWh per person per year
U.K.	55,000 kWh per person per year
Third World	3,000 kWh per person per year

Perhaps expectedly, first comments suggested that the situation was not so alarming as had been presented and that diverting scarce research resources into renewable energy sources at this time might not be in the best interests of mankind. For example, coal reserves for hundreds of years are available. Other points made highlighted arguments surrounding fuel cells as a method of extending the life of fossil fuel reserves, based on their potentially higher energy conversion efficiency. However, many points raised during the discussion lent support to the view that we, mankind, through a mixture of misunderstanding and self-interest, had a blind belief that, when all else fails, some new source of everlasting energy will suddenly become available.

Turning to the consideration of specific sources it was noted that although the total solar energy reaching the earth is enormous (twice the annual world consumption every hour) the peak power density is only 1 kW per square metre, so collection is not easy. The Solar Industry requires a fully sealed battery, efficient at both accepting and delivering energy with a low self-discharge rate. At the present time solar modules are expensive and are usually used only in locations remote from the main power grid. Because of the cost, primary batteries or secondary batteries – charged off site – are often preferred. It appears at the moment that the lead-acid battery is most likely to meet the storage requirements for solar-powered energy sources. High energy density, though uppermost in people's minds,was considered – on balance – to be less important than cost.

Considerable discussion on the interface between battery and photovoltaic systems then followed. It was argued that the two technologies neither get together nor do they consistently base their approach on an overall system concept. Not for the first time the Battery Industry was accused of insularity. The Battery Industry claimed that the Solar Power Industry should put its own house in order and stipulate exactly what it wants in the way of a storage battery. These points, having been made quite forcibly, hopefully bode well for the future.

The expectation that photovoltaic costs will shortly fall below battery costs was expressed and was particularly interesting since, at present, the cost of a solar array is normally twice that of the storage battery.

Hydro-electric systems were next considered and it appears at present that there is little demand for battery support in such systems.

The Tidal scheme was apparently regarded as a very high cost system. Although there is a 240 MW plant in France very little development appears to be taking place.

There was little time for discussion of wind-powered energy sources but it was felt that storage batteries with similar characteristics to those in use for solar power would be suitable for these applications.

Brief mention was made of the use of plants as an energy source but it was clear that the use of batteries for storage in such systems is unlikely.

When discussing special needs it emerged that there is a clear market for solar array plus storage battery systems to provide power supplies for radio and television receiving sets in countries such as Indonesia and Kenya.

The conclusions that can be drawn are that there is a considerable divergence of opinion regarding the whole question of renewable energy requirements. The Battery Industry however, can do much to facilitate the development of solar power sources and accordingly, co-operation between the various disciplines involved should be encouraged.

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SECONDARY ALUMINIUM – METAL SULPHIDE BATTERIES WITH MOLTEN $NaAlCl_4$ ELECTROLYTE

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ABSTRACT

A preliminary evaluation has been made on rechargeable battery systems of the type

$$Al/NaCl\text{-}AlCl_3/MeS_x$$

where MeS_x is a transition metal sulphide.

The cathodes consisted of metal sulphides of approximate compositions corresponding to TiS_2, Cr_2S_3, FeS, $NaFeS_2$, CoS_2, NiS, Ni_3S_2, and MoS_3. Based on general observations of the test batteries, proposed cell reactions together with the open circuit voltages (OCV), semitheoretical energy densities and percent utilisations of active materials are given. It is not yet possible to determine practical attainable maximum energy densities, partly because the cell designs were not optimized. Most promising cycling behaviour was obtained with FeS, $NaFeS_2$, CoS_2, Ni_3S_2 and MoS_3 as cathode materials. A cell with Ni_3S_2 was cycled about 1600 times. The largest semi-theoretical energy density 930 $Wh\,kg^{-1}$ was obtained with the $Al/NaCl\text{-}AlCl_3/CoS_2$ battery with OCV = 1.38 Volt and in which the cathode reaction was a reduction of CoS_2 to Co(metal). For some of the battery systems, charge and discharge curves obtained using a newly developed microprocessor-controlled battery testing system are presented.

INTRODUCTION

The need for better secondary batteries for load-levelling purposes and electric cars is well-known. In order to achieve the highest possible energy density, most research work has been concerned with alkali-metal anodes. Since aqueous electrolytes cannot be used, and organic electrolytes have insufficient electrical conductivity, molten salts or solid electrolytes need to be used. The $Li/LiCl\text{-}KCl/FeS_x$ (Barney *et al.*, 1983) and also the sodium-sulphur systems have been thoroughly investigated, but severe problems, including the very high temperature of operation, still remain unsolved.

In spite of its low equivalent weight (9g/eq.) compared to lithium (7g/eq.) and sodium (23g/eq.), very little interest has been shown in batteries with aluminium anodes. The easy processing, low price and lack of environmental hazards also makes aluminium an interesting candidate for secondary battery development. Previously, attempts have been made to make rechargeable batteries with aluminium anodes, NaCl-$AlCl_3$ electrolytes and chlorine gas (Giner and Holleck, 1972) or elemental sulphur (Rédey *et al.*, 1975) as cathode material. Only one system with metal sulphide cathodes has been investigated, namely Al/NaCl-$AlCl_3$/FeS_2 (Koura, 1980; Koura *et al.*, 1980; Koura and Inoue, 1981a, b). This paper describes our preliminary work on the Al/NaCl-$AlCl_3$/MeS_x system employing different transition metal sulphides as cathode materials.

GENERAL CONSIDERATIONS

The molten NaCl-$AlCl_3$ electrolyte near equimolar composition consists of the compound $NaAlCl_4$ which has a freezing point of 156.7°C (Berg *et al.*, 1984).

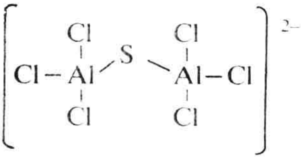
Owing to its high electrical conductivity, $0.44\Omega^{-1}cm^{-1}$ at 175°C (Hjuler *et al.*, 1984) its water-like viscosity (Carpio *et al.*, 1981) and its low vapour pressure (Hjuler *et al.*, 1982), this ionic liquid is well-suited for use as an eloctrolyte in high energy-density batteries. The near equimolar composition melt consists of Na^+, $AlCl_4^-$ and smaller amounts of Cl^- and $Al_2Cl_7^-$ ions. Melts with a mole fraction of $AlCl_3$, X_{AlCl_3}, higher or lower than 0.5 are called (chloro-) acidic or basic, and melts with $X_{AlCl_3} = 0.5$ are called neutral.

The solubility of elementary sulphur in a NaCl-$AlCl_3$ melt saturated with NaCl is less than 2.1×10^{-2} mole S per kg solvent at 175°C (Marassi *et al.*, 1976). The solubility increases with temperature and increases notably with increasing content of $AlCl_3$ (Huglen *et al.*, 1978). Further, sulphide-containing species are very soluble (several moles dm^{-3}) in basic NaCl-$AlCl_3$ melts and less soluble in acidic melts (Berg *et al.*, 1980). The solubility is probably caused by an acid-base reaction such as

$$\mathrm{AlCl_4^- + S^{2-} \rightarrow \text{“}\,AlSCl_{4-\eta}^{(3-\eta)-}\,\text{”} + \eta Cl^-} \tag{1}$$

where η is 2 or 3, depending on the chloride concentration.

The species “$AlSCl_2^-$” and “AlSCl” in eq. 1 are presumably solvated and more or less polymeric, the simplest monomeric structures (Berg *et al.*, 1980) being possibly



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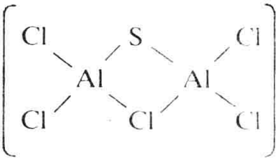

(2)

Melts containing these species are easily obtained in NaCl-$AlCl_3$ melts by reacting aluminium metal, sulphur and NaCl in quantities according to the reaction

$$2Al + 3S + NaAlCl_4 + 2NaCl \rightarrow 3Na\text{“}AlSCl_2\text{”} \qquad (3)$$

These melts are usually water-clear or faintly yellow and, at high sulphur concentrations, highly viscous due to the polymeric properties of Na“AlSCl$_2$”.

EXPERIMENTAL

All weighings and manipulations with these moisture- and oxygen-sensitive compounds were performed in a nitrogen-filled glovebox of our own construction. The average dew point in the box was less than –40°C.

Chemicals

The aluminium anodes consisted of either pure aluminium pieces (99.999%, Atomergic Chemetals), aluminium wire (Baker analyzed Reagent, approx. 99.8%), or ordinary aluminium (99.5%). In order to remove surface impurities, all aluminium was treated with a concentrated NaOH solution, rinsed with water and dipped in a 12:10:3 mixture by volume of 89% H_3PO_4 and concentrated H_2SO_4 and HNO_3 acids to remove traces of oxides.

NaCl (analytical reagent from Riedel-de Häen) was dried for several days at 150°C before use.

$AlCl_3$ (Fluka, $\geq$ 99%, Fe $\leq$ 0.008 %) was purified by heating in vacuum, followed by distillation in contact with aluminium foil and a NaCl-$AlCl_3$ phase. The product consisted of large colourless crystals. Mixed with equimolar amounts of NaCl at 175°C, the final almost colourless $NaAlCl_4$ electrolyte was obtained.

TiS_2 was prepared by continuous reation (Hall and Mickel, 1957) of $TiCl_4$ vapour (Merck, 99%) and H_2S gas (quality N20 from Alfax, > 99%) at 650°C in a quartz tube. The product was golden green with a sulphur content of 53.7% (theoretical 57.2%), determined by oxidizing sulphide to sulphate by means of Br_2 in CCl_4 and HNO_3, and determining sulphate gravimetrically as $BaSO_4$.

Cr_2S_3 was prepared (Udy, 1956) from anhydrous $CrCl_3$ (Riedel-de Häen) and H_2S gas (>99%) in a quartz tube at 440°C. The material was black and contained some unreacted $CrCl_3$. The chromium content was analysed to be 56.1% (theoretical 52.0%).

Two kinds of *FeS* were used: one was a finely ground powder obtained from sticks of ferrous sulphide (technical, BDH Chemicals); the other kind was a precipitate made from an ammonium sulphide solution (40%,

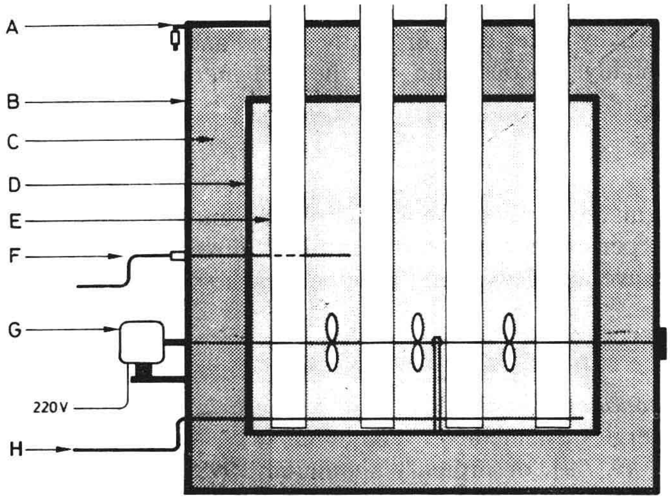

FIG. 1 Oven heated by circulating air.
A: Water-cooled upper plate - made of brass; **B:** Outer aluminium box; **C:** Glass wool insulation, thickness 13cm in the top, elsewhere 10cm; **D:** Inner aluminium box; **E:** Stainless steel tubes, 60mm i.d.; **F:** Platinum resistance thermometer for regulation and measurements; **G:** Electrical motor driving three propellers to achieve small temperature gradients; **H:** 500 Watt heating element, coupled to a PID-regulator.

Riedel-de Häen) and an NH_4Cl-containing solution of $FeCl_3$ (from BDH Chemicals). Both types of FeS-powder contained considerably less Fe than the theoretical value of 63.5%, and they were probably neither stoichiometric nor homogeneous and were perhaps contaminated with water or other impurities.

$NaFeS_2$ was synthesized by thorough mixing of 10g Fe powder, 60g Na_2CO_3 and 60g pure sulphur (analytical grade), followed by heating to about 950°C for 1 to 2 hours. After cooling, the green product was washed with diluted NaOH and filtered off, washed with ethanol and carefully dried in vacuum at about 100°C. The dark brown final product was extremely sensitive (pyrophoric) to atmospheric air. The Fe-content was 32.5% (theoretical 39.1%).

CoS_2 was made by precipitation of aqueous Co(II) chloride solutions with $(NH_4)_2S$ solutions and contained typically 50.6% S (theoretical 52.1%).

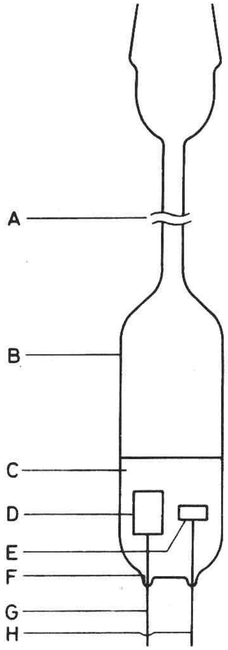

FIG. 2 Sealed battery cell, type A1.
A: Sealing position; **B:** Pyrex glass ampoule; **C:** NaCl-AlCl$_3$ electrolyte; **D:** Aluminium anode; **E:** Metal sulphide disc; **F:** Capillary tubes for sealed, vacuum-tight electric connections; **G:** Negative terminal (tungsten wire). **H:** Positive terminal (tungsten wire).

Two kinds of nickel sulphides were used: the first was precipitated from aqueous solutions of $NiSO_4$ (Riedel-de Häen) and Na_2S (Merck) and contained 62.4% Ni (theoretical 64.7%). The other was Ni_3S_2 obtained from Cerac (99.9%) and was used as received. The Ni-content was checked; it was 73.2% Ni (theoretical 73.3%).

MoS_3 was made (Jacobson *et al.*, 1979a) in two steps. $(NH_4)_2 MoS_4$ was precipitated by H_2S gas ($> 99\%$) acting on a solution of ammonium paramolybdat $(NH_4)_6 Mo_7O_{24}.4H_2O$ (from BDH) in aqueous ammonia at ambient temperature. This precipitate was then treated with acid. The Mo content of the final dry product was 48.3% (theoretical 49.9%).

Furnaces

Most of the experiments were carried out in an oven with circulating heated air constructed in this laboratory. Fig. 1 shows the construction. A

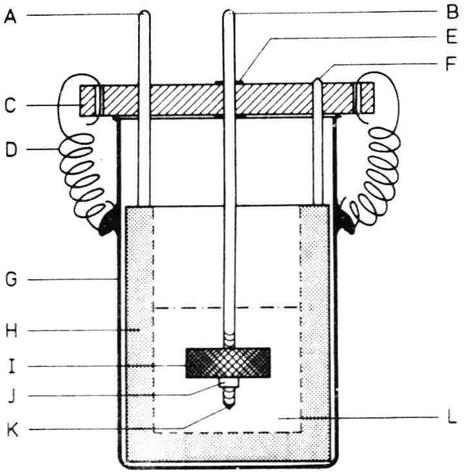

FIG. 3 Battery cell, beaker type B1, for use in the glovebox furnace. **A:** Stainless steel pin (negative terminal) connected to the aluminium anode; **B:** Stainless-steel pin (positive terminal) to support the sulphide cathode; **C:** Slate lid; **D:** Springs to fasten the slate lid to the beaker; **E:** Circular spring to keep the terminal B in the right position; **F:** Stainless steel pin to centre the cathode; **G:** Pyrex glass beaker; **H:** Cup of aluminium, 99.5% (anode); **I:** Metal sulphide disc (cathode); **J:** Nut to fasten the sulphide disc; **K:** Thread; **L:** NaCl-$AlCl_3$ electrolyte.

glass furnace equipped with a water-cooled glass jacket (Brekke *et al.*, 1979) was used in some of the experiments. This allowed inspection without affecting the temperature equilibrium.

Testing of the beaker type cells (B1), see Fig. 3 and later, was conducted in a furnace incorporated in the floor of the glovebox. The furnace was of the earlier described type (Andreasen *et al.*, 1977) but with a 120mm internal diameter and a length of 400mm.

Construction of the test batteries

Cathodes were normally made by pressing powders of the metal sulphides containing usually 50 to 100mg steel-wool in a die of 13mm diameter (Beckmann D-01) or a die (constructed in this laboratory) of 25mm diameter which could contain, for example an expanded nickel mesh *including* an outer terminal. The pellets were pressed by means of a hydraulic press (type C-30 from RIIC, London). The average force applied was approximately 5 tons, and the thickness of the discs was from 2 to 5mm. Certain discs were heat-treated in vacuum at 250 to 300°C in order to improve their mechanical stability. Discs with no outer terminal had a