



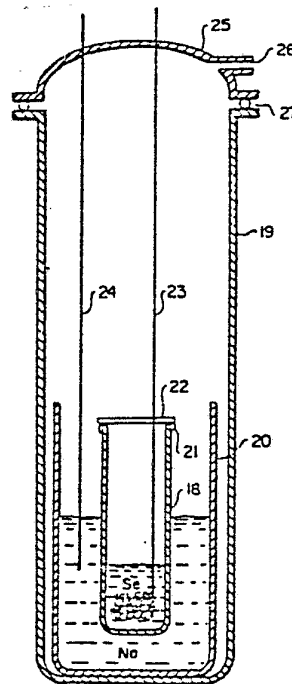
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<p>(21) International Application Number: PCT/US83/00289 (22) International Filing Date: 4 March 1983 (04.03.83) (31) Priority Application Number: 355,528 (32) Priority Date: 8 March 1982 (08.03.82) (33) Priority Country: US</p> <p>(71) Applicant: CERAMATEC, INC. [US/US]; 163 West 1700 South, Salt Lake City, UT 84115 (US). (72) Inventors: BRITT, William, S. ; 2765 Blue Spruce Drive, Salt Lake City, UT 84117 (US). MILLER, Gerald, R. ; 584 DeSoto Street, Salt Lake City, UT 84103 (US). VIRKAR, Anil, V. ; 1875 Suzette Circle, Salt Lake City, UT 84106 (US). (74) Agents: BRITT, William, S. et al.; Trask & Britt, P.O. Box 1978, Salt Lake City, UT 84110 (US).</p>		<p>(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), JP, LU (European patent), NL (European patent), SE (European patent).</p> <p>Published <i>With international search report.</i></p>

(54) Title: IMPROVED ELECTROCHEMICAL CELL UTILIZING SELENIUM AS AN ELECTRODE-REACTANT

(57) Abstract

An improved high temperature electrochemical cell employing a molten sodium metal anode (10), a solid ceramic electrolyte (11) containing mobile sodium ions and a molten selenium cathode (13).



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IMPROVED ELECTROCHEMICAL CELL UTILIZING
SELENIUM AS AN ELECTRODE-REACTANT

Background of the Invention

5 Field: This invention relates to high temperature electrochemical cells employing molten electrodes, and particularly to an electrochemical cell employing sodium as an anode and selenium as a cathode.

10 Prior Art: Various types of electrochemical cells employing molten alkali metal electrode-reactants are known. These cells generally employ an ionically conductive ceramic, for example, beta"-alumina, or glass membranes through which alkali metal ions pass. Secondary batteries employing a molten sodium electrode and a molten sulfur electrode are described in U.S. Patents 3,404,035 and 3,404,036 to Kummer et al. A primary battery having a molten sodium reactant in contact with a sodium ion conductive ceramic membrane is described in U.S. Patent 3,458,356 to Kummer et al.

20 Selenium has been mentioned in various patents, for example, U.S. Patents 3,476,602; 3,672,995 and 3,679,480 to Brown et al and U.S. Patent 4,015,054 to Clever et al, as a cathodic material. In Fischer, U.S. Patent 4,127,705, selenium is described as an additive to the cathode. The mention of selenium has generally been in reference with other catholytes in which sulfur is the preferred cathodic material and selenium, tellurium, tetra-
25 cyanoethylene, para-thiocyanogen, ferricyanide and the like are optical cathodic materials. As indicated in the Clever et al patent, a fused salt is interposed between the anodic material and the electrolyte. All experimentation
30 referenced in the prior art patents known to applicant is related to sulfur as a cathodic material.



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A great deal of work has been done on the sodium-sulfur battery. It has shown great potential as a power source for electric vehicles because of its power to weight ratio, which is about ten times better than conventional lead-acid batteries. The sodium-sulfur battery also has the potential of long life when operated within the proper parameters. These proper parameters may, however, be a hindrance to wide-spread commercialization of the sodium-sulfur battery.

The sodium-sulfur battery based upon present performance, is projected to give a compact size vehicle a range of about 200 miles, moderate acceleration and a recharge time of about eight hours. Such a vehicle would be a suitable urban vehicle. However, improvement of the range, acceleration and recharge rate would enhance considerably the usefulness of electric vehicles. The operating parameters of the sodium-sulfur battery remain an obstacle to such improvements.

The range of an electric vehicle is limited by the capacity of the battery powering it. The capacity is a function of degree of discharge. The sodium-sulfur battery can be discharged until the sulfur is converted to Na_2S_3 (at 350°C). If it is discharged further, certain sulfides of sodium, normally Na_2S_2 , are precipitated which become and remain insoluble even upon recharge. Repeated "deep-discharge" of a sodium-sulfur battery will ultimately render the battery useless.

The project recharge rate for a sodium-sulfur battery, i.e., overnight recharging, is acceptable for an urban car with a range of 200 miles. However, it would be desirable for long distance travel to have a vehicle with a range of 300 to 400 miles, or more, with a recharging rate of one hour, which would permit recharging during meal breaks. Rapid recharging is limited by the critical



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current density which the solid electrolyte will tolerate. Electrolyte tubes of B"-alumina, a particularly effective sodium ion conductor, have excellent life so long as recharging of a cell containing such electrolytes is done at a current density less than the critical current density. Critical current density increases for B"-alumina electrolytes as temperature increases. Similarly, conductivity (the inverse of resistance) increases for such electrolytes with increasing temperature. Increasing the operating temperature of a sodium-sulfur cell above the usual temperature of 350°C is detrimental in other respects. Sulfur presents a troublesome corrosion problem at 350°C; at higher temperatures the corrosion problem is greatly exacerbated. Sulfur containing cells may become pressurized at more elevated temperatures. For a number of reasons, a pressurized cell is generally undesirable.

Objects of the Invention

It is an object of the instant invention to provide a less corrosive electrochemical cell which may be deep-discharged.

It is a further objective to provide an electrochemical cell utilizing a molten anode and cathode for operation at very high temperatures, for example, temperatures in excess of 500°C.

Another object of the invention is to provide an electrochemical cell having a cathodic material which enhances the conductivity of the electrolyte and whose reaction products with anode material produces an electronically conductive material.

Description of the Drawings

FIG. 1 is a schematic view of a sodium-selenium secondary battery cell;



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FIG. 2 is a schematic view of a sodium-selenium secondary battery cell of an inverted construction;

FIG. 3 is a graphical representation of the open-circuit voltage of a sodium-sulfur cell at various stages of discharge;

FIG. 4 is a graphical representation of the open-circuit voltage of a sodium-selenium cell at various stages of discharge.

Description of the Invention

An improved electrochemical cell employing a molten sodium anode and a molten selenium cathode has been invented. The improved cell employs a solid, impervious cation conducting membrane, i.e., electrolyte, of beta-alumina or beta"-alumina. The sodium anode may contain minor quantities of selenium or minor quantities of selenium may be contained within the electrolyte, as described in copending U.S. Patent Application Serial No. 310,859 of Virkar and Miller, incorporated herein by reference.

It has been found that a sodium-selenium electrochemical cell may be operated efficiently without many of the disadvantages which accompany sodium-sulfur electrochemical cells. The sodium-selenium cell, because of the lower corrosiveness of the selenium and its lower vapor pressure may be operated at much higher temperatures. For example, normal operation of a sodium-sulfur cell is 350°C with a practical upper limit of a sodium-sulfur cell of about 400°C, (sulfur boils at 444°C), while sodium-selenium cells may be operated effectively at temperatures over 500°C and up to about 600°C (selenium boils at 685°C) without becoming pressurized. Pressurization of cells containing molten materials is undesirable because of the possibility of an explosive-type failure of the cell.



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Constructing a cell to withstand pressure involves the use of thicker walled materials. A thick-walled ceramic electrolyte such as beta"-alumina is undesirable inasmuch as the resistance of electrolyte increases proportionately with cell wall thickness.

Electrochemical cells of the sodium-sulfur and the sodium-selenium type have increased efficiency with increased temperatures, however, because of some of the problems, e.g., excessive corrosion and pressurization, attendant at elevated temperatures with sodium-sulfur cells, such cells are operated at relatively low temperatures, i.e., generally at 350°C and lower. Also, degradation of the electrolyte has been of concern in sodium-sulfur cells while the operation of the sodium-selenium cell has been found to involve less electrolyte degradation. Selenium, either in small quantities in the anodic material or in the electrolyte, as disclosed in copending U.S. Patent Application Serial No. 310,859, or present as substantially the sole constituent of the cathode diminishes the problems of degradation of the electrolyte. The inclusion of selenium as substantially the sole cathodic constituent or as the major constituent of the cathode appears to impart a beneficial effect to the beta-alumina or beta"-alumina electrolyte.

Small quantities of various ingredients may be added to the selenium cathode for purposes of assisting in control or adjustment of viscosity or to enhance further the conductivity of the cathode. Gallium or thallium may be advantageously utilized to lower the viscosity of molten selenium.

A further advantage of sodium-selenium cells involves the formation of sodium-selenides, which impart better conductivity to the cathode than does the formation of sodium-sulfides in a sodium-sulfur cell. Thus, in a



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sodium-selenium cell less difficulty is encountered in conducting electrons from the cathode chamber to an external circuit. Also, because of the less corrosive nature of selenium in comparison to sulfur, metal containers such as stainless steel and the like can be used as the container for the cathode compartment. Such containers are more electrically conductive and cheaper to construct than the more complicated containers required to contain sulfur at equivalent temperatures.

EXAMPLE

A cell assembly was constructed according to FIG. 2.

A small quantity of selenium was placed inside a B"-alumina tube having a nominal wall thickness of about 1.6 mm and a resistivity of about 5 ohm-cm. A molar excess of sodium was placed in the external annular cavity. The cell assembly was then placed in an oven and maintained at a temperature in excess of 350°C until the sodium and selenium were molten.

A series of voltage readings at varying temperatures were taken at various states of discharge. The voltage readings were taken at intervals of about 10°C beginning at 350°C and continuing to about 470°C. The following table sets forth voltages at representative temperatures.

Table I
Voltage

<u>T°C</u>	<u>Initial</u>	<u>Na₂Se₆</u>	<u>Na₂Se₄</u>	<u>Na₂Se₃</u>
350	1.92	1.90	1.64	1.65
400	1.90	1.89	1.78	1.72
450	1.87	1.87	1.79	1.73



Table II

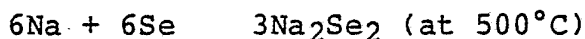
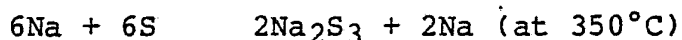
FIG. 3 - Avg. V = 1.94

FIG. 4 - Avg. V_{350°C} = 1.80

FIG. 4 - Avg. V_{450°C} = 1.81

5 Although the initial open voltage of a sodium-selenium cell is less than that of a sodium-sulfur cell, the sodium-selenium voltage stays relatively constant even to deep-discharge while the voltage of a sodium-sulfur cell decreases significantly with discharge. Also, a sodium-selenium cell may be discharged to a very deep-discharge and then substantially fully recovered by recharging. This is in contrast to sodium-sulfur cells which do not recover fully if deep-discharged (at deep-discharge various sodium sulfides precipitate which do not resolubilize upon recharging). A sodium-selenium cell has greater capacity because of its ability to be deep-discharged, which also makes it more volumetrically efficient than a sodium-sulfur cell.

10 The power output of a sodium-selenium cell per mole of sodium is greater per discharge cycle than for a sodium-sulfur cell. The following equations are useful in assessing power output.



15 It may be observed from these equations that in a sodium-sulfur cell which discharges to the Na₂Se₃ state, the reaction, based upon available sodium, is only 67% as complete as the sodium-selenium reaction. During recharging, the cell is usually only charged to about 90% of its original condition, i.e., about 10% of the anolyte remains in the catholyte. Thus, the capacity for a

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sodium-sulfur cell is about 60% while the capacity of a sodium-selenium cell is about 90% of theoretical.

Based upon these equations and the average voltages from FIGS. 3 and 4, a calculation of useful energy storage may be made. Assuming an appropriate cell design to accommodate a one ohm load, the average current generated ($I = E/R_2$) is 1.94 amps for the Na-S cell and 1.8 amps for the Na-Se cell, while the power generated, $P = EI$, is 3.76 and 3.24 watts, respectively. Assuming a constant discharge rate to achieve complete discharge over a time period T, then the energy generated per discharge cycle is 2.26 watt hours (60% x 3.76) for a Na-S cell and 2.90 watt hours (90% x 3.24) for a Na-Se cell. Thus, the energy capacity of a sodium-selenium cell (at 500°C) per mole of sodium is about 25% greater than that of a sodium sulfur cell (at 350°C). The heat loss of such a sodium-selenium cell will be slightly greater than for a similar sodium-sulfur cell since it is operated at a higher temperature.

It should be noted that in addition to being more deeply discharged than a sodium-sulfur cell, a sodium-selenium cell may be more advantageously recharged. In sodium-sulfur cells it is prudent to recharge only to the Na_2S_5 state, i.e., recharging to the state of free sulfur being present if the catholyte is not efficient. In a sodium-selenium cell, more sodium may be returned to the anode chamber during recharging without having free selenium in the catholyte melt inasmuch as Na_2Se_6 is formed, which contains less sodium proportionately than Na_2S_5 .

A comparison of various physical properties of sodium, sulfur and selenium are set forth in the following table.



Table III

<u>Element</u>	<u>Melting Point</u>	<u>Boiling Point</u>
Selenium	217°C (423°F)	684.9°C (1265°F)
Sulfur	112°C (235°F)	444.6°C (832°F)
5 Sodium	97.8°C (208°F)	892°C (1638°F)

From a comparison of boiling points, it may be seen that the sodium-selenium cell may be operated at very high temperatures, e.g., up to 600°C, without experiencing unduly high vapor pressures within the cell. It is very
10 desirable to operate at a relatively high temperature because the resistance of the solid electrolyte to ion flow significantly decreases with increasing temperature.

A sodium-selenium cell operated at high temperatures facilitates fast discharge and rapid discharge
15 inasmuch as the resistance of the electrolyte is low. Electrolyte life is also enhanced inasmuch as the critical current density increases substantially with increasing temperature. Thus, at high temperatures the electrolyte membrane tolerates a large current density without substan-
20 tial degradation.

The preferred electrolyte for this invention is a heterogeneous ceramic of an aluminum oxide matrix containing mobile sodium ions. Such ceramics as beta and
35 beta"-alumina are exemplary of such ceramics with beta"-alumina being the preferred electrolyte material.

A selenium core sodium-selenium secondary battery cell is illustrated in FIG. 1. The liquid sodium
30 anodic material 10 is contained within a solid tubular electrolyte 11, e.g., a beta"-alumina tube, and a metal housing 12 to provide an expansion cavity for the liquid sodium. In the practice of the instant invention, selenium may be added to the cell so it is present adjacent the anodic interface of the electrolyte as a coating

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upon the electrolyte or absorbed into the surface of the electrolyte. Liquid selenium 13 forms the cathodic reactant of the cell. The canister or container 14 enclosing the selenium should be at least mildly corrosion resistant as well as electronically conductive, e.g., stainless steel. An electrically insulating seal header 15 physically separates the anode and cathode materials. The seal header, preferably of alpha-alumina, must be corrosion resistant as well as being ionically and electronically nonconductive. The electrical leads to a load are provided by electrically conductive members 16 and 17, which interact with the anode and cathode, respectively.

The cell utilized in the work described herein was constructed similar to the cell illustrated in FIG. 2. The electrolyte tube 18 is constructed of beta"-alumina. The outer container 19 is of Vycor and the intermediate container is an alpha-alumina crucible. The electrolyte is sealed by a glass seal 21 to an alpha-alumina header 22. Wire-type electrodes 23 and 24 of molybdenum contact colten selenium and graphite felt in the electrolyte cavity and molten sodium in the annular cavity external to the electrolyte.

The outer container 19 is secured to a cover 25, which has an evacuation part 26. The cover 25 and container 19 are bolted together (bolts not shown). An O-ring seal 27 seals the space between the cover 25 and container 19.

In commercial applications, the container 18 is of stainless steel, or the like, and serves as an electrode. The stainless steel container and the electrolyte tube are joined as a unit at the top of each by an alpha-alumina header. Typically, graphite felt serves as an electron conductor in the cathode chamber, e.g., in contact with the selenium. As noted elsewhere herein,



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operation of the cell so that only selenides (Na_2Se_6 to Na_2Se_2) are present provides sufficient electroconductivity to eliminate a tightly packed graphic felt insert (which occupies space which would be better occupied by the catholyte) or to permit utilization of a very loose, less dense graphic felt. Also, in the presence of selenium and sodium-selenides other conductive "felts" could be utilized because of the decreased corrosiveness of selenium in comparison with sulfur.

The inverted design illustrated in FIG. 2, otherwise denominated as the sulfur core cell in sodium-sulfur battery terminology, is illustrated herein with selenium contained within the tubular electrolyte and sodium in the outer chamber. This cell configuration has been utilized with sodium-sulfur cells in order to confine the corrosive sulfur within the corrosion resistant ceramic electrolyte tube and sodium, which is less corrosive, can be contained within a mild steel outer container. This configuration, for a sodium-sulfur cell, requires a non-corrosive current-collector assembly for contact with the sulfur because of the corrosiveness of the sulfur and the sulfur vapors within the cathode chamber. Inasmuch as selenium is much less corrosive than sulfur, many advantages exist for an inverted design for sodium-selenium cells. A sodium-selenium cell of inverted design is easier to construct inasmuch as the sodium selenides formed in the cathode chamber are sufficiently conductive to permit use of a simple current collection, e.g., of ferrous metal.

The presence of selenides other than sodium selenide may further enhance the conductivity of the catholyte. A mixture of selenium and bismuth selenide, for example, may be advantageously used. Such mixtures are significantly more conductive than selenium alone or selenium-sodium selenide mixtures. Other metal selenides



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may be substituted for bismuth, although bismuth is preferred.

5 It has been found from the instant invention that the features of greater volumetric efficiency, rapid charge and rapid discharge (high power output), ability to deep-discharge without loss of capacity and simplified cell design offset any lower voltage output from a sodium-selenium cell.



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Claims

1. An electrochemical cell comprising:
a molten sodium electrode-reactant;
a solid ceramic electrolyte containing mobile sodium ions;
and
molten selenium as the electrode-reactant separated from
the sodium by the solid electrolyte.

2. The electrochemical cell of Claim 1 wherein
the electrolyte is beta-alumina or beta"-alumina.

3. The electrochemical cell of Claim 1 wherein
minor quantities of selenium are present at the
sodium-electrolyte interface.

4. The electrochemical cell of Claim 1 wherein
the solid ceramic electrolyte contains selenium therein.

5. An electrochemical cell comprising:
a molten sodium electrode-reactant;
a ferrous metal outer container current collector to con-
tain said sodium;
a tubular, sodium ion conductive ceramic electrolyte con-
tainer within said outer container and in
substantial contact with said sodium;
a molten selenium electrode-reactant contained within said
electrolyte container;
a ferrous metal current collector having substantial con-
tact with said selenium.

6. The electrochemical cell of Claim 5 wherein
said selenium is present substantially as sodium
selenides.



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7. The electrochemical cell of Claim 5 wherein the temperature of said molten selenium is at least 500°C.

8. The electrochemical cell of Claim 5 wherein a porous electroconductive material is present in said selenium.



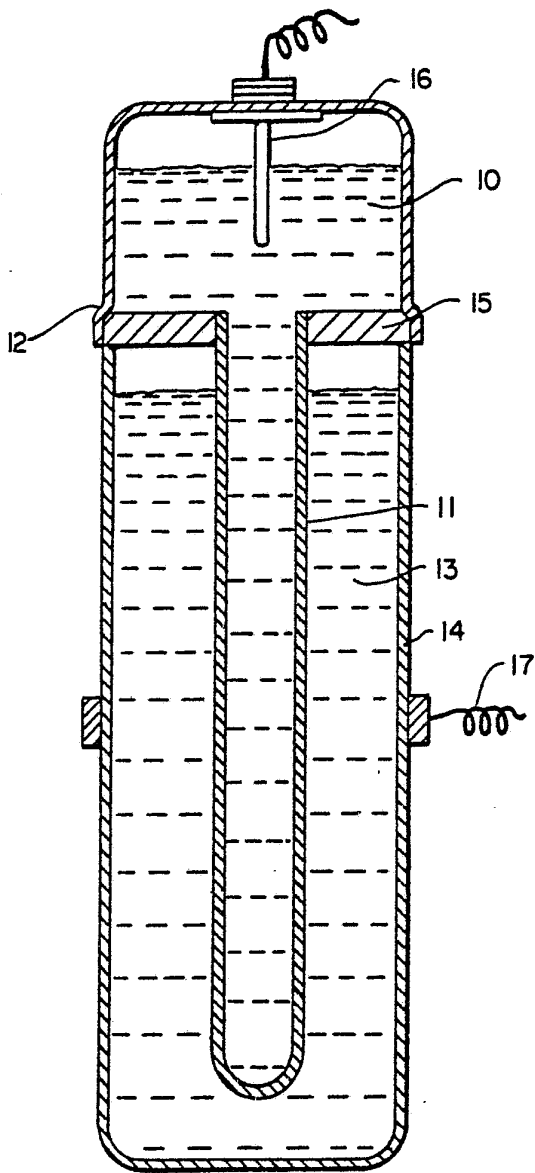


Fig. 1

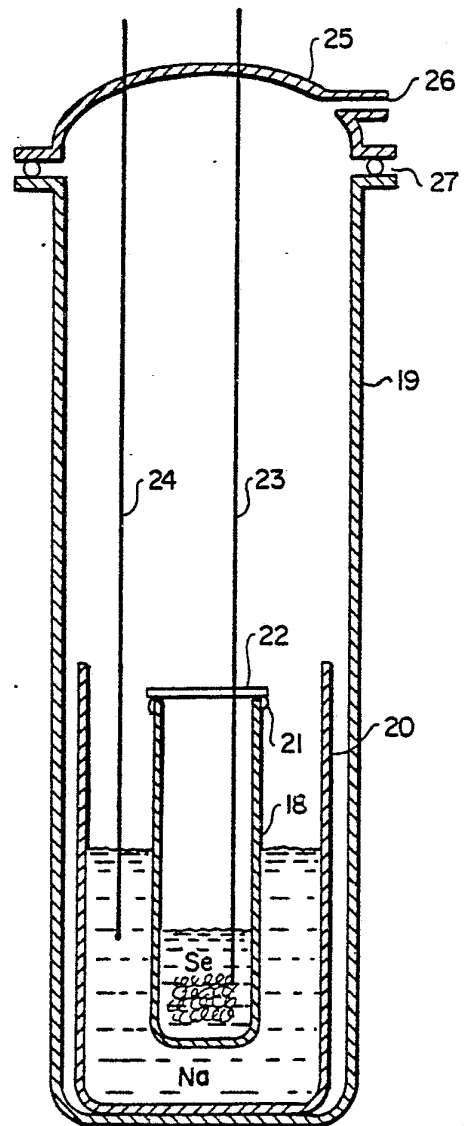


Fig. 2



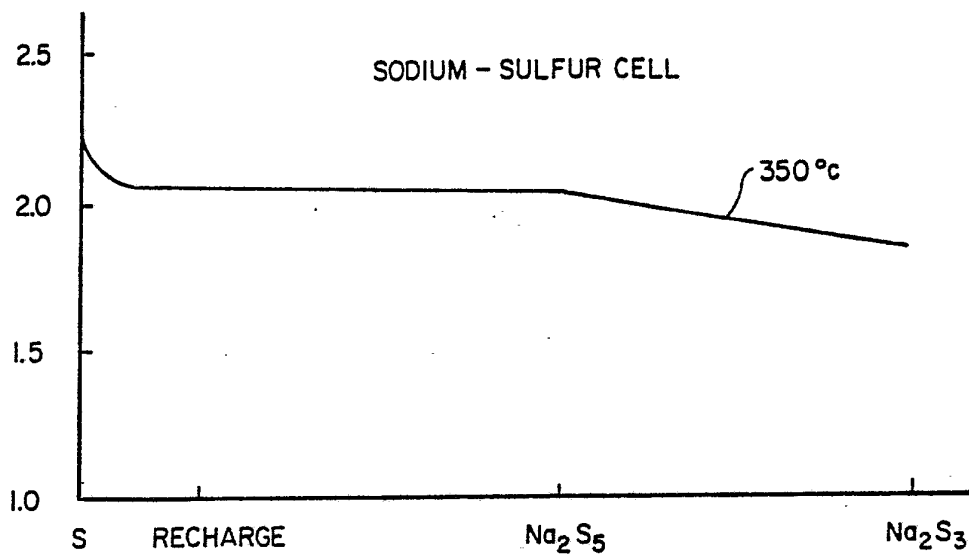


Fig. 3

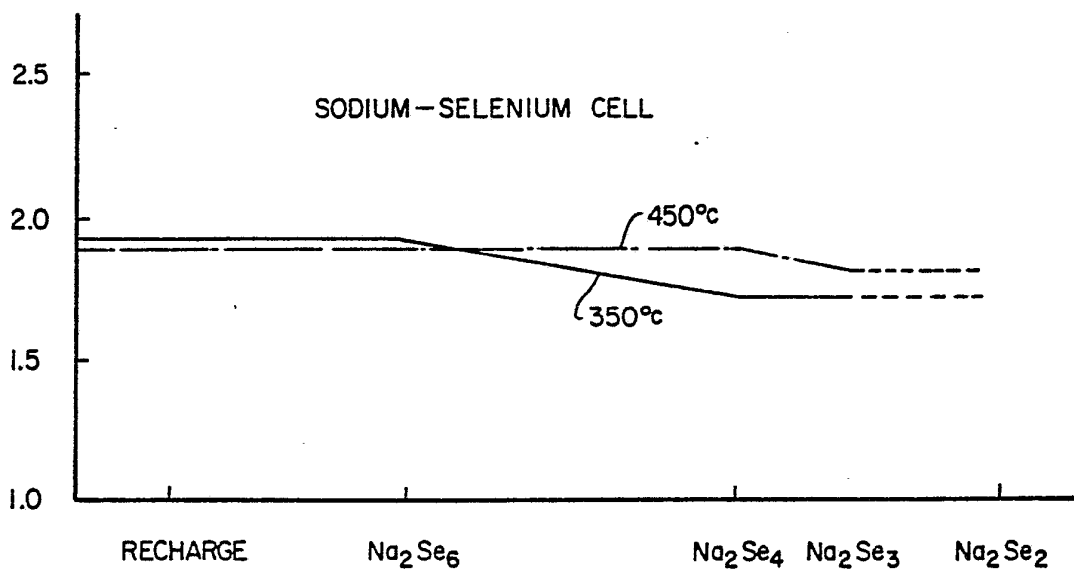


Fig. 4



INTERNATIONAL SEARCH REPORT

International Application No PCT/US83/00289

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. ³	H01M 4/36, 4/48, 6/20	
US. CL.	429/104	
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
US	429/104, 102, 193	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	US, A, 4,015,054, (CLEAVER et al) March 29, 1977	
A	US, A, 3,476,602, (BROWN et al) November 4, 1969	
A	US, A, 3,672,995, (BROWN et al) June 27, 1972	
A	US, A, 3,679,480, (BROWN et al) July 25, 1972	
A	US, A, 4,024,319, (KAGAWA) May 17, 1977	
A	US, A, 4,127,705, (FISCHER et al) November 28, 1978	
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IV. CERTIFICATION		
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10 December 1982	<div style="font-size: 1.5em; font-weight: bold; margin: 0;">31 MAY 1983</div>	
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