(51) International Patent Classification 5 : H01L 35/02	A1	(11) International Publication Number: WO 93/09570
		(43) International Publication Date: 13 May 1993 (13.05.93)

(54) Title: CAPACITIVE THERMOELECTRIC DEVICE
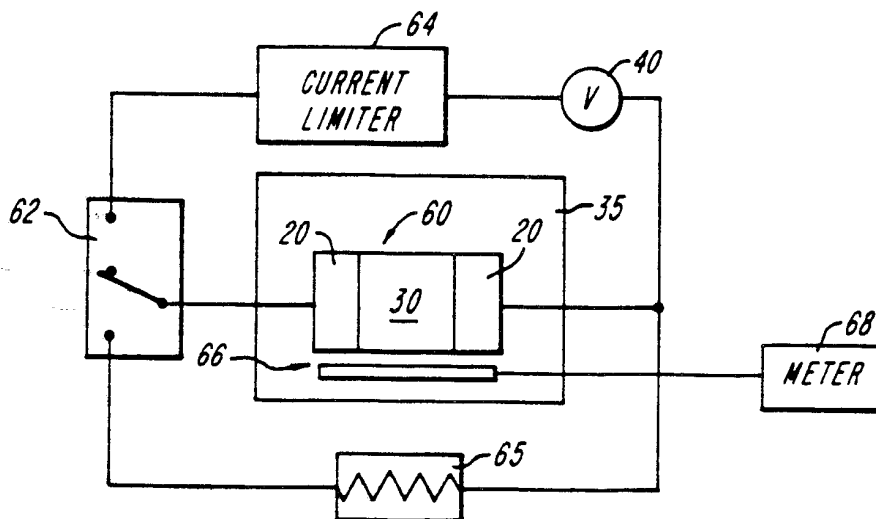
(57) Abstract

A thermoelectric device for cooling a mass; the device comprising a capacitor having two electrodes and being in thermal contact with the mass to be cooled. The capacitor produces a cooling effect when it is repeatedly isothermally charged and adia-batically discharged.

CAPACITIVE THERMOELECTRIC DEVICE

This application is a continuation-in-part application of U.S.S.N. 07/784,544, filed October 29, 1991.

5
Background of the Invention

This invention relates to solid state thermoelectric devices, and particularly relates to thermoelectric device materials.

Conventional solid state thermoelectric devices operate based on the Peltier effect, which is achieved by passing an electric current through a junction of

10 dissimilar metals. Such a device is typically constructed from two semiconductor blocks, one being a heavily doped n-type material and the other being a heavily doped p-type material. The blocks are connected electrically in series and thermally in parallel. In this arrangement, heat is absorbed at a so-called cold junction of the semiconductor blocks and is transferred to a so-called

15 hot junction at a rate proportional to the current passed through the semiconductor blocks. When the current is applied in series with the n-type and p-type blocks, electrons pass from a low energy level in the p-type material to a higher energy level in the n-type material. This diode-like action causes heat to be removed from the cold junction of the two blocks and pumped through the

20 blocks (in parallel) to the hot junction.

Bismuth telluride is currently the most popular semiconducting material used for Peltier effect thermoelectric devices. It exhibits high mechanical strength, high electrical conductivity, and low thermal conductivity, three desirable characteristics for a thermoelectric device. Commercially

25 manufactured bismuth telluride Peltier devices can achieve temperature differentials of approximately 65°C, and can pump tens of watts of heat.

Summary of the Invention

In general, in one aspect, the invention features a thermoelectric device comprising two electrodes separated by an electrolyte. Each of the electrodes

30 comprises a crystalline material characterized by the presence of van der Waals

channels, the van der Waals channels being capable of accommodating the electrolyte within the channels to form a double layer of charge at interfaces of the van der Waals channels and the electrolyte when a voltage is applied between the two electrodes. The thermoelectric device exhibits a temperature

5 decrease in a two-stage cooling process comprising application of a voltage between the electrodes to thereby form the double layer and replacement of the voltage with a load through which the double layer is discharged. Using selected materials, the thermoelectric device of the invention exhibits a 0.5°C temperature decrease for each two-stage cooling process repetition, and thus

10 provides a significant thermoelectric effect. Further detailed descriptions of compounds having van der Waals channels and devices which utilize these compounds are provided in the following applications, all filed of equal date as "Electrolytic Double Layer Capacitor", and hereby incorporated by reference: "Capacitive Thermoelectric Device" and "Energy Storage Device".

15   In preferred embodiments, the voltage application is controlled to charge said double layer isothermally and discharge the double layer adiabatically. Preferably, the crystalline material is a bismuth chalcogenide, and most preferably, each of the two electrodes comprises a monocrystal of the bismuth chalcogenide. In other preferred embodiments, the two electrodes each comprise

20 monocrystalline powder particles of the crystalline material. The van der Waals channels of the crystalline material are adapted to accommodate the electrolyte by a training process comprising intercalation of electrolyte into the channels. Preferably the intercalation is produced by a training voltage sufficiently high as to achieve electrolyte penetration of the van der Waals channels, and most

25 preferably, the training voltage is periodically reversed in polarity between the electrodes.

        In general, in another aspe
ct, the invention provides a thermoelectric device for cooling a mass, the device comprising a capacitor having two electrodes and being thermally coupled to the

30 mass, the capacitor providing a cooling effect when it is repeatedly isothermally charged and adiabatically discharged. Preferably, the capacitor is a double layer capacitor, and more preferably, the capacitor is an electrolytic capacitor.

In general, in another aspect, the invention provides a thermoelectric device comprising two electrodes separated by an electrolyte, each electrode comprising a porous material capable of forming a double layer of charge at interfaces of the porous material and the electrolyte when a voltage is applied

5   between the two electrodes. The device exhibits a temperature decrease in a two stage cooling process comprising application of a voltage between the electrodes to thereby form the double layer and replacement of the voltage with a load through which the double layer is discharged.

In preferred embodiments, the porous material comprises a compound of

10   bismuth chalcogenide, activated carbon, and heat-treated graphite, and preferably, the electrolyte comprises sulphuric acid. Preferably, the voltage application is controlled to charge said double layer isothermally and discharge the double layer adiabatically.

The thermoelectric device of the invention exhibits an accumulated

15   temperature decrease produced by repetitions of a two-stage cooling process, namely charging and discharging. Its compact structure and elegantly simple operation provide significant advantages over conventional thermoelectric devices. Other features and advantages of the invention will become apparent from the following description, and from the claims.

Brief Description of the Drawing

Fig. 1 is a schematic illustration of one embodiment of the thermoelectric device of the invention;

Fig. 2A is a schematic illustration of the device of Fig. 1 at a first stage of

5 training;

Fig. 2B is a schematic illustration of the device of Fig. 2A at a later stage of training;

Fig. 2C is a schematic illustration of the device of Fig. 2A at a final stage of training;

10 Fig. 2D is a schematic illustration of the device of Fig. 2A including the formation of a double layer of charge; and

Fig. 3 is a diagram of an electrical circuit for operating the thermoelectric device of the invention.

Description of the Preferred Embodiment

15 We first present a discussion of the operational theory of the thermoelectric device of the invention. The thermoelectric device of the invention is a capacitive device characterized by the ability to accommodate a very high charge density, and correspondingly high energy storage, and very low internal resistance. The capacitor thereby achieves very high discharge power, and in

20 fact, a discharge rate which is so fast as to be energetically adiabatic. Furthermore, very little resistive, or joule, heating occurs during the discharge process. As will be explained further below, these characteristics of the discharge process are so pronounced as to provide a cooling effect via the following device operation. The capacitive device is first isothermally "charged"

25 to a very high charge density, thus in an isothermal manner, whereby the entropy of the device is decreased. The capacitive device is then adiabatically discharged, whereby the entropy of the device is increased, necessarily resulting in a temperature decrease, or cooling, of the device. The charge/discharge cycle may thus be understood as a classical Carnot cycle, in which the cycle

30 temperature is directly related to the cycle kinetics and changes in entropy.

The inventors herein have recognized that while theoretically, any capacitive structure is capable of thermoelectric cooling, particular capacitive

schemes and particular device materials are best-suited for achieving

thermoelectric cooling. Based on the operational theory explained above, a

capacitive cooling device ideally comprises a capacitive structure capable of very

high charge density accumulation and very low internal resistance; in

5   particular, the resistance of the capacitor electrodes ideally is held low. Given

these criteria, electrolytic double layer capacitors, known to be capable of quite

high charge accommodation, have been identified as providing a superior

capacitive structure for a cooling device. Accordingly, the cooling device of the

invention is based on a double layer capacitive structure.

10   As an example of the charge density accumulation limitations of capacitors,

the capacitance of a typical parallel plate capacitor is given by: analyze the

operational electrical properties of this structure, consider first

$$C = \varepsilon_0 \varepsilon S/d,$$

where ε_0 is a constant, ε is the dielectric constant of the medium between the

15   capacitor electrodes, S is the surface area of the capacitor electrodes, and d is

the width of the medium separating the electrodes. The charge density

accommodation, i.e., the capacitance, of a given capacitor is thus limited by the

geometry, i.e., the surface area, the electrode spacing, the material properties of

the electrodes, and the medium separating them.

20   The definition of capacitance for a double layer capacitor is further

specified by the structure of the charged double layer and its geometry. This

double layer comprises charge accumulation on the electrode surface and

accumulation of ions at the electrode surface-electrolyte interface. Thus, for

double layer electrolytic capacitors, the width d in the capacitance equation is

25   given by the distance between the centers of the two regions constituting the

double layer. This distance is on the order of angstroms, thereby providing a

very large capacitance value for a given capacitor surface area.

The capacitive cooling device of the invention provides an even greater

increase in capacitance (and charge density accommodation) by providing an

30   increase in surface area of the capacitor electrodes over conventional double

layer electrodes, and through proper selection of the electrode material and the

electrolyte. Furthermore, as explained in detail below, the selected electrode

materials and electrolytes provide a dramatically low internal resistance, a parameter which is critical to the cooling device operation.

In the capacitive cooling device of the invention, increased electrode surface area is obtained using a particular class of materials, namely intercalation

5   compounds, which are characterized by a layered crystalline structure. The crystal layers of intercalation compounds comprise planes of molecules or atoms which are weakly bound together and separated from each other by van der Waals regions. These van der Waals regions form anisotropic channels in the crystal lattice between the planes of molecules or atoms, resulting, in effect, in a

10   "two dimensional" crystal structure. Intercalation materials typically exhibit on the order of 10^6-10^7 layers per millimeter of material thickness. Due to the weak van der Waals force between the crystal layers, the lattice channels can accommodate the physical introduction, or so-called intercalation, of a guest intercalant species into them.

15   The inventors herein have recognized that a particular type of intercalation compound, namely bismuth chalcongenides, including Bi_2Te_3 and Bi_2Se_3, are particularly well-suited for providing van der Waals channels as an extension of electrode surface area. Electrodes composed of these materials, when used in combination with a suitable electrolyte, generate a highly uniform double layer

20   of a desirable structure. As is well-known to those skilled in the art, bismuth chalcongenides exhibit a layered crystalline lattice which is layered at the molecular level, each layer being separated by a van der Waals channel having a width on the order of 3-4 Å. Further material properties of bismuth chalcogenides are given in the copending United States Patent Application

25   entitled "Layered Crystalline Material Capable of High Guest Loading," herein incorporated by reference, being filed on the same day as the present application. Of the materials surveyed, the inventors have found that of the bismuth chalcogenides, Bi_2Te_3 exhibits the best electrical conductivity, and correspondingly, the lowest resistance, and is thus most preferable as an

30   electrode material, while Bi_2Se_3 exhibits a lower conductivity, and thus is less preferable as an electrode material.

It must be emphasized that while the bismuth chalcogenides are

understood to provide superior electrical properties, other intercalation materials may be employed in the capacitive cooling device of the invention, and materials characterized by other crystal structures which provide high charge density may also be utilized as an electrode material. For example, activated

5 carbon, a porous material, may also be utilized as an electrode material; the porous nature of activated carbon enhances the material's effective surface area.

In one embodiment of the capacitive cooling device of the invention employing intercalation electrode materials, the van der Waals regions of the electrode material are employed such that the surfaces of the crystal lattice

10 channels, although internal to the electrode material, contribute to the overall electrode surface area, and thereby dramatically increase the effective electrode surface area beyond that of its macroscopic surface. As described in detail below, surfaces of the van der Waals channels of the electrode material are capable of forming a double layer with an electrolyte in the same manner as the

15 electrode macroscopic surface forms a double layer. Recognition and exploitation of this physical process has enabled the inventors herein to achieve the significant cooling capability in the cooling device of the invention as a result of increased charge density accommodation.

Depending on the intercalation electrode material and the electrolyte

20 selected for the cooling device, the van der Waals channels of the electrodes may need to be manipulated, or "trained" to effectively accommodate the electrolyte within them. The condition for this requirement is based on the structural dimensions of the van der Waals channels and the solvated complex radius of the electrolyte's solvated ions. If the complex radius of the solvated ions is

25 larger than the width of the van der Waals channels, then the electrolyte will not be able to penetrate the channels and no double layer will be formed within the channels. Accordingly, a material having van der Waals channel widths which are less than the solvated ionic radius must be trained to accommodate the larger ions, and thereby trained to accommodate the electrolyte itself. The

30 van der Waals channel width of bismuth chalcogenides is too narrow for electrolytes of interest to penetrate them, and thus a "training" of bismuth chalcogenide is required. A detailed training sequence is described below.

Electrode materials, like activated carbon, which are not intercalation compounds, do not require such a training process, because they do not contain van der Waals regions. As explained above, activated carbon provides an enhanced surface area with the surfaces of its internal pores, which

5   accommodate electrolyte to form a double layer of charge.

The charge density capacity and the internal resistance of electrode materials, and particularly intercalation materials, are dramatically impacted by the purity and defect density of the chosen material. This is manifested in the degree of ability to manipulate van der Waals channels to increase electrode

10   surface area. Impurities and crystal lattice defects distort the geometry, as well as the field characteristics, of the van der Waals channels, rendering them less accessible to intercalating species, degrading the channel surface structure and thus degrading the electrical and mechanical properties of the channels. Accordingly, it is ideally preferred that the material chosen for the capacitor

15   electrodes be prepared using unique processes, developed by the inventors herein, yielding a highly pure and as defect-free as possible material. To that end, the following single crystal growth process is preferred for bismuth chalcogenide materials. Alternative processes, providing less than ideally pure and defect-free material, may nonetheless be acceptable for particular cooling

20   device applications. Those skilled in the art will recognize critical material parameters and corresponding performance results.

In the preferred intercalation compound preparation process, stoichiometric quantities of highly purified (99.9999% pure) bismuth and tellurium (or other selected chalcogenide) are first charged into a quartz ampoule. If necessary, the

25   materials are zone refined before use. Off-stoichiometry results in an n- or p-doped material with the resultant degradation of the lattice structure and the associated performance. The ampoule is evacuated to 10^{-7} mmHg and backfilled to a pressure of 10^{-3} mmHg with a small amount of inert gas, such as argon, or a reducing gas, such as hydrogen (3-10 cycles), and then sealed. Hydrogen is

30   particularly preferred because it reacts with oxygen during processing to prevent oxidation and decrease the segregation of chalcogenide by reducing its vapor pressure.

A highly homogeneous polycrystalline material is prepared in a first processing step. The sealed ampoule is placed in a furnace at room temperature and heated to a temperature 5-10°C above its melting point. The ramp rate, temperature and reaction time are dependent upon the final compound. The

5 reaction conditions are listed in Table I for the preparation of polycrystalline Bi_2S_3, Bi_2Se_3, and Bi_2Te_3. The temperature of the furnace over the entire length of the ampoule is controlled to within ±0.5°C. Careful and accurate control of the temperature is important because of the high volatility of chalcogenides. Temperature variations along the ampoule length causes segregation of

10 chalcogenide which leads to off-stoichiometry. To optimize the temperature control along the length of the ampoule, a long furnace can be used. Additional heating coils can be used at furnace ends to reduce the temperature gradient at the furnace exits.

Table I. Processing conditions for polycrystalline material.

15

processing conditions	Bi_2Te_3	Bi_2Se_3	Bi_2S_3
heating rate to T_{liq} (°C/h)	30	20	15
exposure time (h)	10	15	20
at T_{liq} + 10°C			
cooling rate (°C/h)	50	40	35

20

During the last hour of reaction time, the ampoule is agitated or vibrated

25 to insure complete mixing of the ampoule components. The ampoule vibration is in the range of 25-100 Hz and is accomplished by fixing one end of the ampoule to an oscillation source. Any conventional vibration means is contemplated by the present invention. After reaction is complete, the ampoule is cooled at a slow controlled rate.

30 Once a homogeneous polycrystalline material is obtained, it can be further processed into a highly defect-free bismuth chalcogenide single crystal. Any known method of growing single crystals can be used, such as Bridgeman techniques, Czolchralski process and zone refinement (recrystallization). In particular zone refinement has proved to be highly effective in obtaining high

35 purity single crystals.

Zone refinement is preferably carried out in a quartz boat containing a

seed crystal of the desired lattice structure, e.g., the hexagonal lattice structure. It is recommended that clean rooms levels of Class 100 be maintained. The seed crystal is oriented in the boat such that crystal layers are horizontal. The entire apparatus should be shock-mounted to insulate against environmental

5   vibrations. The boule of polycrystalline material is positioned in surface contact with the seed crystal.

The furnace comprises two parts, an outer furnace for maintaining an elevated temperature along the entire boule length and a narrow zone movable in a direction for heating a small portion of the polycrystalline material. The

10   outer furnace is maintained at 35°C below the melting point and the zone, which is 2-3 cm in length, is held at 10°C above the melting point of the polycrystalline material. Unlike for the preparation of the polycrystalline material, in the first processing step described above, the boule can be rapidly heated to the operating temperature. The zone is initially positioned at the

15   seed crystal/boule interface and this region is heated to the melting point of the material. The zone is moved slowly down the length of the boule. Zone travel rate varies with composition, and exemplary rates are shown, along with other processing parameters, in Table II. Zone travel rate is an important processing parameter. If it is too great, crystallization is incomplete and defects are

20   formed. If it is too slow, layer distortions result. The lower portion of the heat-treated boule in contact with the quartz boat is preferably removed before use.

Table II. Processing conditions for hexagonal single crystal growth.

processing conditions	Bi_2Te_3	Bi_2Se_3	Bi_2S_3
boule temperature	M_p - 35°C	M_p - 35°C	M_p - 35°C
zone temperature	M_p + 10°C	M_p + 10°C	M_p + 10°C
zone travel rate	8 mm/hr	6 mm/hr	3 mm/hr
cooling rate	50 °C/hr	40°C/hr	35°C/hr

The above process can be modified slightly to produce crystals of rhombohedral structure, in which case a rhombohedral seed crystal is used in the zone refinement process. In addition, to obtain rhombohedral crystals, the

35   furnace temperature is held at 30°C below the melting point and the zone is

maintained at the melting point of the polycrystalline material.

Preferably, a monocrystalline intercalation compound, and most preferably, bismuth chalcogenide, is grown using the process described above to produce monocrystalline electrode structures. For example, as one embodiment

5   of the invention, monocrystalline bismuth chalcogenide electrodes are produced having a rectangular geometry with sides of 4 millimeters-long and 5 millimeters-long, and having a thickness of between 0.5-1 millimeters. It is preferable to metalize one of the faces of the monocrystalline material which is perpendicular to the plane of the van der Waals channels within the crystal.

10   This metalization may consist of, for example, a nickel paste, which is spread on the crystal to form a 10-20 micron-thick metal layer. The metalization provides both a good electrical contact to the crystalline piece and enhances the rigidity of the crystalline piece.

Alternatively, the monocrystalline bismuth chalcogenide material may be

15   ground into a powder for forming the electrodes; such a powdered material is more easily manipulated than the single crystal material. The crystal grinding process may be carried out using, for example, a ball milling device, or other grinding device, to produce single crystal particles each having a diameter of preferably approximately 70 microns. Other particle diameters may be more

20   preferable in specific instances. The crystal particles are then mixed with an appropriate compound to bind them together. While the binder acts, in effect, to "glue" the particles together, it must not completely electrically insulate the particles from each other. The binder material is selected according to the electrolyte. When an aprotic electrolyte solvent is used, the binder preferably

25   consists of a 3% aqueous solution of carboxymethylcellulose, in which the particles are mixed; for other electrolytes, alternative binding agents, e.g., a 5% polyethylene dispersion in normal hexane, may be used. The resulting powder-binder mixture is placed into an electrode mold and then dried at room temperature. The electrode geometry, as determined by the mold, may be, for

30   example, disc-shaped, as is conventional for capacitors, with an electrode thickness of between 0.3-1 millimeters. Alternative electrode geometries are also feasible.

The grinding process described above produces some amount of crystal damage, and corresponding crystal defects. However, because of the weakness of the van der Waals attractive force between the crystal layers of intercalation compounds, these compounds cleave readily along the axis of the channels

5 without much danger of lattice damage or distortion.

The inventors herein have also developed a preferable process for producing electrodes of material combinations of bismuth chalcogenides, activated carbon, and heat treated graphite. In this scheme, a bismuth chalcogenide, such as Bi_2Te_3, may be present in the range of from 0 to 100%.

10 The activated carbon material (ACM) may also be present in the range of 0 to 100% and the heat treated graphite (HTG) may be present in the range of from 0 to 40% of the ultimate composition. An electrode with higher performance but with higher cost will include a higher proportion of the bismuth chalcogenide whereas an electrode with lower performance and lower cost will include a

15 higher proportion of the ACM. The particular proportions chosen will thus be based on a cost-performance analysis. The composition is held together with a binder such as polytetrafluoroethylene (teflon).

If the electrode is to include a bismuth chalcogenide such as Bi_2Te_3, the process described above is employed to produce monocrystalline powder

20 particles. The starting material for the ACM is a cellulose fiber. The cellulose fiber is heat treated at 800-950°C for one to two hours in an oxygen free environment. Thereafter, it is activated in a steam atmosphere at 800-900°C for two to three hours. The material is then crushed into particles having diameters in the range of 4-8 mm and a length of 0.5 mm. This material will

25 have a specific surface area of 1300-2500 m^2/g. The heat treatment of the cellulose fiber material will result in an 85-90% carbon content.

Production of the heat treated graphite (HTG) begins with crystalline flake graphite having an ash content of not more than 2%. This material is ground and sorted to have a maximum diameter of 200 μm. The particulate

30 material is then heat-treated in an electric furnace at a temperature in the range of 2200-2500°C in a vacuum atmosphere. The preferred vacuum is 10^{-4} mmHg. The material is maintained in the furnace for a time sufficient to

reduce residual ash content to less than 0.1%. After this heat treatment, the powdered material is sifted in a vibration sifting device, resulting in particles having a diameter in the range of 80-200 μm.

5   The selected binder material, for example, polytetrafluoroethylene, is first processed in a mixer to obtain a bulk volume of 3-5 cm²/g. The binder is added to the powder material in a quantity not to exceed 20 wt% of the electrode weight.

Once the starting materials are prepared, the following steps are carried out to fabricate an ACM electrode. First, the monocrystal bismuth chalcogenide

10   powder, if any is to be included, the heat treated graphite, and the teflon are put into a mixer and mixed for 2-3 minutes at a speed of rotation not less than 4,000 rpm. Thereafter the selected quantity of ACM is added and the mixing process is continued for another 2-3 minutes at the same speed to obtain a material having a bulk volume of 4.3-4.7 cm³/g. A suitable material begins with

15   97% HTG and 3% teflon; ACM is then added to provide 80% of the total weight.

This electrode material is then compressed onto a metallic substrate in a hydraulic press with a compression pressure of approximately 270 MPa. A suitable electrode size is 10 cm by 10 cm by 0.1 cm. A suitable substrate

20   material is perforated nickel foil having holes whose diameter is in the range of 0.7-1.0 mm. The distance between the holes is in the range of 0.6-0.8 mm. Other perforation schemes are also acceptable. A preferred thickness of the metallic substrate is 0.1 mm.

After the electrode composition is pressed onto the metallic substrate, the

25   resulting electrode is annealed for 1-2 hours at a temperature of 100-140°C in a chamber evacuated to 10^{-1} mmHg.

After annealing, the electrode is impregnated with a suitable electrolyte such as a 28-30% water solution of potassium hydroxide. The electrode is immersed in the electrolyte at room temperature under pressure for

30   approximately 5-10 minutes.

Using a suitable electrode production process, including either of the processes described above or another suitable process, the capacitive cooling

device of the invention is assembled into the following scheme. Referring to Fig. 1, in the preferred device configuration 60, two identical electrodes, most preferably being bismuth chalcogenide electrodes 20, are separated by an electrolyte 30. The electrolyte 30 suitably consists of an aqueous solution of,

5   e.g., alkali, or 1.0 M of LiClO$_4$ in propylene carbonate, using bismuth chalcogenide electrodes. In this case, a separator, consisting of 2 layers of non woven polypropylene, each layer 100 μm-thick, and saturated with the electrolyte, provides mechanical support of the electrolyte. Alternatively, for various electrode materials, the electrolyte may comprises a 1.2 M solution of

10   organic cation of perchlorate in a mixture of propylene carbonate in dimethoxyethane, an aqueous solution of potassium hydroxide, an aqueous solution of single valence metal sulphates, or other aqueous solution. Using the LiClO$_4$ propylene carbonate electrolyte discussed above, a polypropylene separator is suitably impregnated with the electrolyte solution and is positioned

15   between the electrodes 20. Because the separator material adds to the overall internal resistance of the device, the separator thickness should be minimized while at the same time taking dependent device parameters into consideration. The electrodes, held apart by the separator, are inserted into a supporting frame (not shown) and sealed in a pressing form.

20   As explained above, depending on the cooling device electrode material and electrolyte, the material may need to be "trained"; in particular, some intercalation compounds must be trained to allow the electrolyte to penetrate the van der Waals channels and form a double layer of charge with the channels' surfaces. Bismuth chalcogenides, while being preferred for their

25   electrical properties, are one type of intercalation material which requires this training process. Accordingly, "training" is a process, described below, whereby electrolyte (and ions) are driven within the van der Waals channels to facilitate flow of electrolyte into and out of the channels. While the process will be described for this material, it must be recognized that the same procedure may

30   be applied to other materials.

        Referring to Fig. 2A, there is shown a capacitive cooling device 60 having two bismuth chalcogenide electrodes 20a, 20b at the start of the training

process. The dimensions of the electrodes' van der Waals channels 70a, 70b are greatly exaggerated for clarity, and it must be recalled that each electrode is comprised of on the order of 10^6-10^7 such channels. Between the two electrodes is positioned a $LiClO_4$-based electrolyte 30. During the training process, the

5   power supply 40 is set to provide a voltage which is greater than the faraday potential for cation intercalation, and thus the voltage depends directly on the particular combination of device electrode material and electrolyte employed. Given a particularly chosen electrode-electrolyte combination, those skilled in the art will recognize that the corresponding faraday potential may be

10   determined in a standard table of material systems and faraday voltages.

At the start of the electrode training, when a voltage above the faraday voltage is applied to the device, the electrode 20b connected to the positive terminal of the power supply accumulates a positive surface charge. The surfaces of the van der Waals channels 70b of the electrode likewise accumulate

15   this positive surface charge. Correspondingly, both the macroscopic surface and the surfaces of the van der Waals channels 70a of the electrode 20a connected to the negative terminal of the power supply accumulate a negative surface charge.

In response to this surface charge configuration, free Li^+ ions 72 readily

20   intercalate the negatively charged electrode 20a, because of the favorable charge and energy configuration, and because their ionic radius is relatively smaller than the width of the van der Waals channels. In addition, solvated Li^+ complexes 74 move toward the negatively charged electrode surface and solvated ClO_4^- complexes 76 move toward the positively charged electrode surface. The

25   positively charged electrode's van der Waals channels 70b, being 3-4 Å-wide (as occurring before the training process) are too small for the ClO_4^- complexes to penetrate within them; the solvated Li^+ complexes, however, do to a small degree penetrate the 3-4 Å-wide channels 70a of the negatively charged electrode 20a, effectively being transported along with the free Li^+ ions to the

30   electrode surface and within the electrode channels. As a result, the solvated Li^+ complexes slightly widen the channels that they partially enter in the negatively charged electrode.

In order to cause the solvated Li^+ complexes to penetrate the opposite electrode 20b, the polarity of the power supply is reversed. Then, the accumulated surface charge distribution reverses; the previously positively charged electrode now accumulates negative surface charge, and attracts the

5   free Li^+ ions 72 and solvated complexes 74. The free Li^+ ions 72 readily intercalate the channels and the solvated complexes 74 again partially enter the corresponding van der Waals channels, and thereby slightly widen the channels.

Referring to Fig. 2B, repetition of this process of voltage polarity switching progressively widens the van der Waals channels of each of the

10   electrodes 20a, 20b. Throughout the process, the voltage may be increased, depending on the initially applied voltage, to thereby increase the attraction of the ions and electrolyte to the van der Waals channels. At an intermediate point in the training process, as depicted in the figure, the solvated Li^+ complexes 74, as well as the free Li^+ ions, will be able to completely penetrate

15   the widened channels 70b of the electrode 70b, which is shown to be currently negatively charged. The solvated ClO_4^- complexes, being of a larger size than the solvated Li^+ complexes, will not yet be able to completely penetrate the channels of the currently positively charged electrode 70a, however.

At the end of the training process period, referring to Fig. 2C, both the

20   solvated ClO_4^- complexes 76 and the solvated Li^+ complexes 74 are able to completely penetrate the van der Waals channels 70a, 70b, of both electrodes, 20a, 20b. As shown in Fig. 2D, at this time, electrically neutral electrolyte (including both ClO_4^- complexes 76 and Li^+ complexes 74) is thereby able to completely penetrate the van der Waals channels and create an electric double

25   layer of charge 80, 82 and 84, 86 at the electrode-electrolyte interface throughout the van der Waals channels of each electrode, in a manner similar to that which occurs at the macroscopic surface of the electrodes. This penetration of electrolyte throughout the crystal channels forms the basis for achieving dramatic charge density increases that result in the cooling effect achieved by

30   the invention.

The extent of training required to achieve penetration of the electrolyte within the electrodes' van der Waals channels is critically dependent on the

particular combination of electrode material and electrolyte employed. The
width of the electrode van der Waals channels before undergoing any training
process and the radius of the solvated complexes in the electrolyte determine the
training required; the larger the complex radius and the smaller the van der

5   Waals channels' width, the longer the training time requirement. For the
electrode material Bi_2Te_3 and an $LiClO_4$-based electrolyte, the training
preferably consists of about 20 training cycles of approximately 30 minutes each,
where the polarity of the power supply is reversed with each cycle. For specific
capacitive device requirements, this training may be adjusted, however. With

10   less training, a lower degree of electrolyte penetration within the channels
would be achieved, and a correspondingly lower double layer capacitance would
result. Thus, for achieving the maximum possible capacitance of a given
electrode, the training should be maximized. Those skilled in the art will
recognize that a preferable training procedure may be empirically determined

15   for a given electrode-electrolyte combination and charge density accommodation
goal.

Alternative training processes are within the intended scope of the
invention. For example, the voltage polarity may be maintained constant in the
above process, or a charge-discharge process may be employed to widen the van

20   der Waals channels. In such a process, a voltage above the faraday potential is
applied between the electrodes, in the manner discussed above, for a period of
time, and then the capacitor is discharged across an appropriate load. If the
voltage polarity is maintained constant during this process, or if the voltage
polarity is not switched during the training process first described, one of the

25   electrodes may not achieve widened channels, depending on the electrode
material and electrolyte composition. For example, using Bi_2Te_3 electrodes and
a $LiClO_4$-based electrolyte in a training procedure in which the voltage polarity
is constant, the electrode having the negative polarity will be intercalated with
free and solvated Li^+ complex (and thereby accommodate electrolyte), but the

30   electrode of positive polarity will not have the benefit of free Li^+ ions and
complexes beginning to open its lattice channels, and thus the solvated ClO_4^-
complexes will not widen those channels to accommodate electrolyte; as a result,

-17-

the electrode of positive polarity will not provide the extended van der Waals surfaces.

Of particular importance is the fact that the training process does not deform or distort the crystal planes of the layered crystalline electrode material to any significant extent. The extent of crystal plane deformation is related to the starting purity and defect density of the electrode material, as well as other properties resulting from the growth process; fewer initial defects in the crystal result in fewer crystal plane deformation sites caused by the training. With little or no crystalline plane distortion at the end of training, the electrodes' van der Waals channel surfaces are uniform and stable, and can correspondingly charge and discharge the double layer in a short time period. In addition, the internal resistance of the material is maintained very low. These conditions provide for the adiabatic discharge mechanism relied on by the cooling device of the invention. Also of importance is the fact that the after the training process widens the van der Waals channels to accommodate the electrolyte, the channels do not later shrink to their original width.

It should be emphasized that alternative materials, like compounds including activated carbon, are also suitable electrode materials and do not require a training process.

Referring now to Fig. 3, the cooling device of the invention is operated in the following configuration. The capacitive device structure 60 is thermally isolated from the ambient via a calorimeter 35, or any suitable insulating container. The device is connected in a parallel charging-discharging circuit via, for example a switch 62. This circuit is external to the calorimeter 35. The charging circuit comprises a power supply 40 and an electrical control component 64, e.g., a current limiter, for limiting the speed with which the power supply charges the double layer of the capacitive device. The discharging circuit comprises an appropriate load 65, e.g., a wire, resistor, or other load element. The load element is suitably selected based on the charge density accumulation of the capacitive device to achieve the highest possible discharge speed. A thermocouple device 66 may be positioned in proximity to the cooling device 60 to measure the cooling effect. Such a thermocouple device might

typically include a meter 68 for indicating the cooling effect measurement.

In operation, the capacitive structure 60 is first connected to the power supply via an appropriate control of the switch 62, at which time the capacitive structure accommodates a charged double layer. The current limiter 64

5 produces a "trickle charge" effect and thereby controls the speed of the charging operation such that it proceeds slowly enough for isothermal conditions to be maintained at the device. A resistor or transistor-based device may suitably be used as a current limiter. Once the capacitive structure has accumulated a characteristic charge density, the switch 62 is controlled to discharge the

10 capacitive structure across the load 65. Due to the very high charge density and very low internal resistance of the capacitive structure, and using a preferably low load resistance, the structure discharges at a speed approaching adiabatic conditions. As a result, during the discharge operation, the temperature of the capacitive structure decreases. Repetition of the charge-discharge process

15 results in accumulation of this cooling effect.

Based on thermodynamic principles, the cooling mechanism results from the adiabatic entropy increase produced when the capacitive structure is discharged. As required by the second law of thermodynamics, an adiabatic increase in entropy results in a temperature decrease. The isothermal

20 capacitive charging process results in an ordering, and corresponding entropy decrease, which is, in effect, released during the discharge process. Based on this phenomena, it is recognized that electrode materials exhibiting a high degree of order are more effective in the cooling device than materials of lesser degrees of order. "Degree of order" is here meant to describe the impact of

25 crystal purity, defect density, uniformity, and other related structural and electrical properties. For example, a monocrystalline electrode structure is understood to provide a larger entropy change and corresponding temperature decrease than a polycrystalline electrode structure.

A Bi_2Te_3, $LiClO_4$-based cooling device of 20 mm in size has been

30 demonstrated to achieve a cooling effect of 0.5-0.7°C per charge-discharge cycle (each cycle consists of one charging and discharging process). This significant cooling effect is cumulative as cycles are continued, and has been demonstrated

to proceed until the electrolyte froze. Preferably, each charge and discharge phase of each cycle is given 1 second to complete. The superior charge accommodation and low internal resistance of this device are understood to enhance the cooling mechanism--the device charge capacity is between 30-100

5   farads per cubic centimeter and the device internal resistance approaches approximately 0.02 Ω-cm^2. This extremely low internal resistance provides the ability to achieve high power in the capacitor discharge. Theoretically, a monocrystalline capacitor structure of pure and defect-free bismuth chalcogenide would exhibit 1000 farads per cubic centimeter and would provide an even

10   higher discharge rate.

It must be understood that the capacitive cooling device of the invention may employ other materials and electrolytes and still achieve a cooling effect; the device performance is, however, effected by the particularly chosen combination of materials and electrolytes. For example, a cooling device

15   consisting of activated carbon electrodes and, employing, e.g., sulphuric acid as an electrolyte, while still achieving the cooling effect, is somewhat less efficient than a device consisting of bismuth chalcogenide electrodes.

Considering that the Bi_2Te_3, $LiClO_4$-based cooling device achieves a degree of cooling which is great enough to freeze the electrolyte, alternative, low

20   freezing-point electrolyte systems may be employed for appropriate electrode materials. For example, in theory, the use of propylene carbonate, which has a freezing point of -60°C, as an electrolyte would provide the ability to achieve a greater degree of cooling.

The inventors herein have recognized that the cooling capability provided

25   by the capacitive cooling device of the invention may be employed in a myriad of applications where a solid state cooling device is preferable over a conventional condensation-type cooling device. Such applications are characterized by space, weight, power, or material limitations (as in the case of replacements for freon-based systems) and include cooling of, e.g., electronic components, medical

30   equipment, optical fiber systems, food refrigeration devices, chemical analysis devices, and an expansive variety of other systems.

Other embodiments of cooling device materials, training schemes, modes

of operation, and application are intended as included within the spirit and scope of the invention.

What is claimed is:

CLAIMS

1. A thermoelectric device comprising two electrodes separated by an electrolyte, each electrode comprising a crystalline material characterized by the presence of van der Waals channels, the van der Waals channels being capable

5 of accommodating the electrolyte within the channels to form a double layer of charge at interfaces of the van der Waals channels and the electrolyte when a voltage is applied between the two electrodes, the device exhibiting a temperature decrease in a two-stage cooling process comprising application of a voltage between the electrodes to thereby form the double layer and replacement

10 of the voltage with a load through which the double layer is discharged.

2. The thermoelectric device of claim 1 wherein said crystalline material is a bismuth chalcogenide.

3. The thermoelectric device of claim 1 wherein said crystalline material comprises a solid solution of $Bi_x(Te_{3-y}Se_y)$, where x is 1 or 2, and y is 0-

15 3.

4. The thermoelectric device of any of claims 1, 2, or 3, wherein said two electrodes each comprise a monocrystal of said crystalline material.

5. The thermoelectric device of any of claims 1, 2, or 3, wherein said two electrodes each comprise monocrystalline powder particles of said crystalline

20 material.

6. The thermoelectric device of either of claims 1 or 3 wherein said electrolyte comprises a 1.0 M $LiClO_4$ solution in propylene carbonate.

7. The thermoelectric device of either of claims 1 or 3 wherein said electrolyte comprises a 1.2 M solution of organic cation of perchlorate in a

25 mixture of propylene carbonate in dimethoxyethane.

8. The thermoelectric device of claim 1 further comprising a power supply for providing said voltage, means for controlling said voltage application, and resistive means for providing said load.

9. The thermoelectric device of claim 8 wherein said voltage

30 application is controlled to charge said double layer isothermally.

10. The thermoelectric device of claim 9 wherein said double layer discharge through said load is adiabatic.

11. The thermoelectric device of either of claims 1 or 2 wherein said van der Waals channels are adapted to accommodate the electrolyte by a training process comprising intercalation of electrolyte into the van der Waals channels.

5   12. The thermoelectric device of claim 11 wherein said intercalation is produced by the application of a training voltage between said electrodes, said training voltage being sufficiently high as to achieve solvated ionic complex penetration of said channels.

13. The thermoelectric device of claim 12 wherein said training voltage
10 is periodically reversed in polarity between the electrodes.

14. The thermoelectric device of claim 13 wherein said training voltage is increased over time from a first voltage sufficient to produce faradaic processes in the electrolyte to a second voltage sufficient to achieve electrolyte penetration of said channels.

15   15. The thermoelectric device of claim 14 wherein said training voltage is applied to said electrodes for approximately 600 minutes.

16. The thermoelectric device of claim 15 wherein said training voltage is reversed in polarity every approximately 30 minutes.

17. A thermoelectric device for cooling a mass, the device comprising a
20 capacitor having two electrodes and being thermally coupled to said mass, the capacitor providing a cooling effect when it is repeatedly charged and discharged.

18. The thermoelectric device of claim 17 wherein said charging is isothermal and said discharging is adiabatic.

25   19. The thermoelectric device of claim 18 wherein said capacitor comprises a double layer capacitor.

20. The thermoelectric device of claim 19 wherein said capacitor comprises an electrolytic capacitor.

21. The thermoelectric device of claim 19 wherein said capacitor
30 electrodes each comprise a crystalline material characterized by the presence of van der Waals channels.

22. The thermoelectric device of claim 19 wherein said capacitor

electrodes each comprise a porous material.

23. The thermoelectric device of claim 22 wherein said capacitor electrodes each comprise activated carbon.

24. The thermoelectric device of claim 21 wherein said crystalline material comprises bismuth chalcogenide.

25. The thermoelectric device of claim 23 wherein said capacitor electrodes each comprise $(Bi_2Te_3)_x(Carbon)_{1-x}$, where x is 0-1.

26. A thermoelectric device comprising two electrodes separated by an electrolyte, each electrode comprising a porous material capable of forming a double layer of charge at interfaces of the porous material and the electrolyte when a voltage is applied between the two electrodes, the device exhibiting a temperature decrease in a two stage cooling process comprising application of a voltage between the electrodes to thereby form the double layer and replacement of the voltage with a load through which the double layer is discharged.

27. The thermoelectric device of claim 26 wherein said porous material comprises a compound of bismuth chalcogenide, activated carbon, and heat-treated graphite.

28. The thermoelectric device of claim 27 wherein said electrolyte comprises sulphuric acid.

29. The thermoelectric device of either of claims 1 or 26 wherein said voltage application is controlled to charge said double layer isothermally.

30. The thermoelectric device of claim 29 wherein said double layer discharge is adiabatic.

31. The thermoelectric device of either of claims 1 or 26 wherein said device exhibits an accumulated temperature decrease produced by repetitions of said two-stage cooling process.

32. The thermoelectric device of claim 31 wherein one of said repetitions occurs approximately every one second.
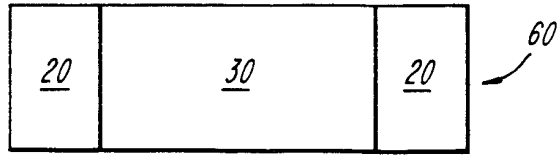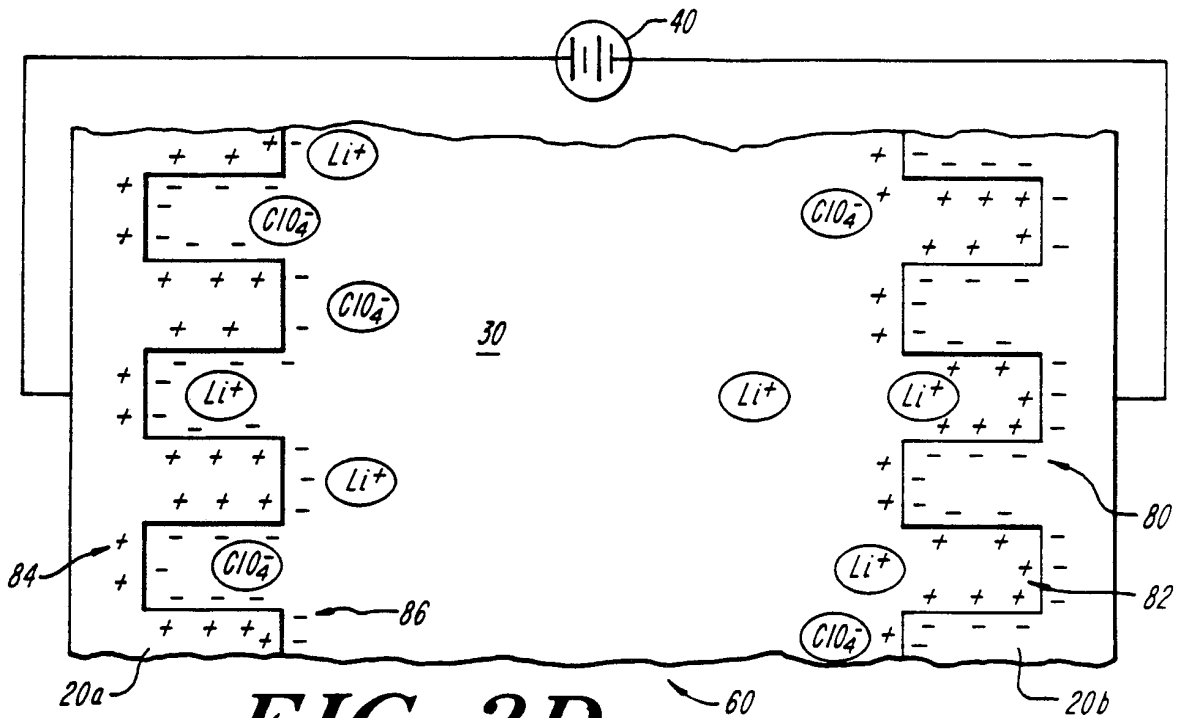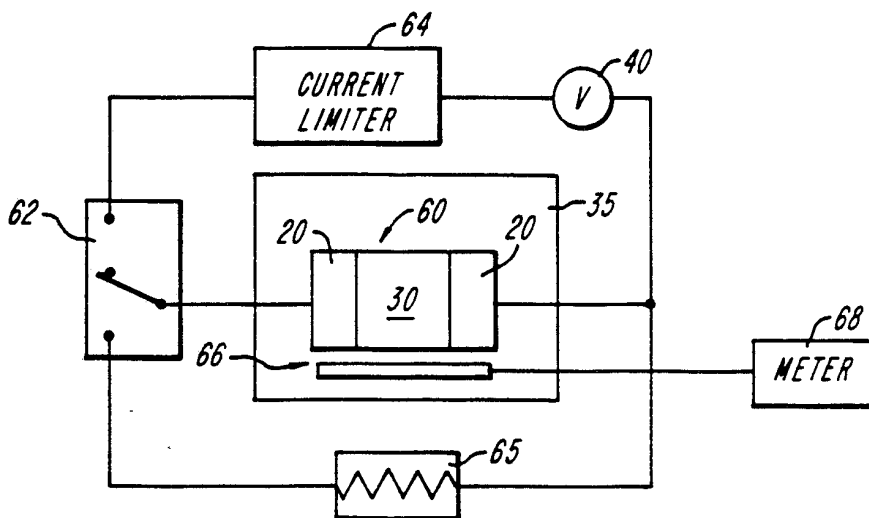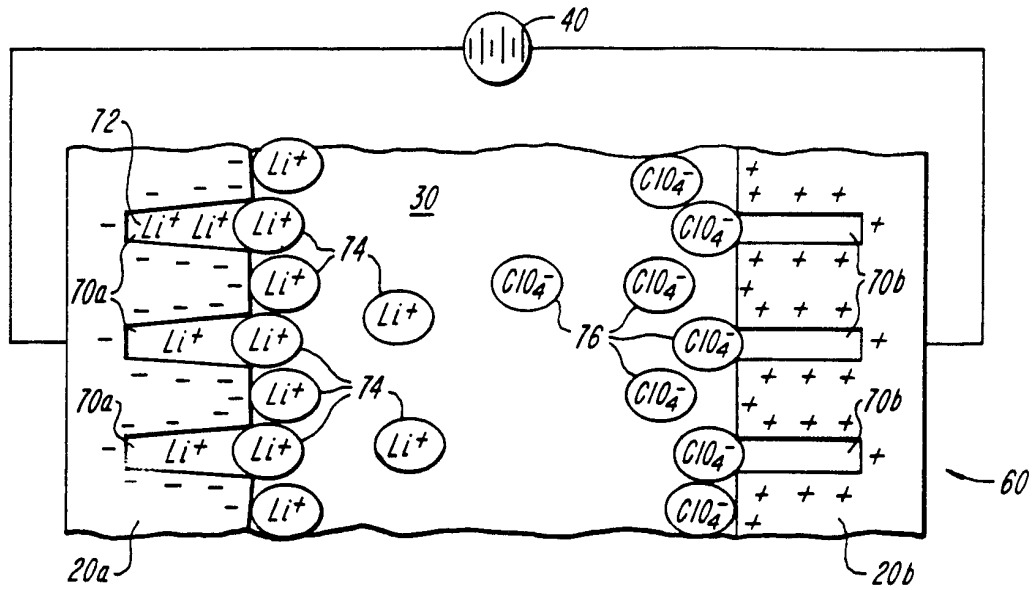
FIG. 1

FIG. 2D

FIG. 3

FIG. 2A
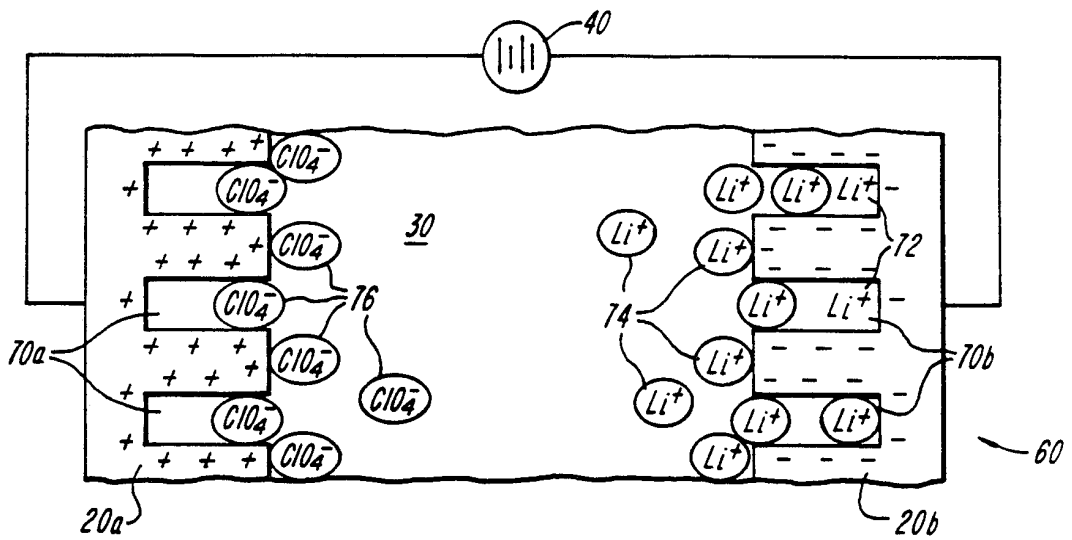
FIG. 2B
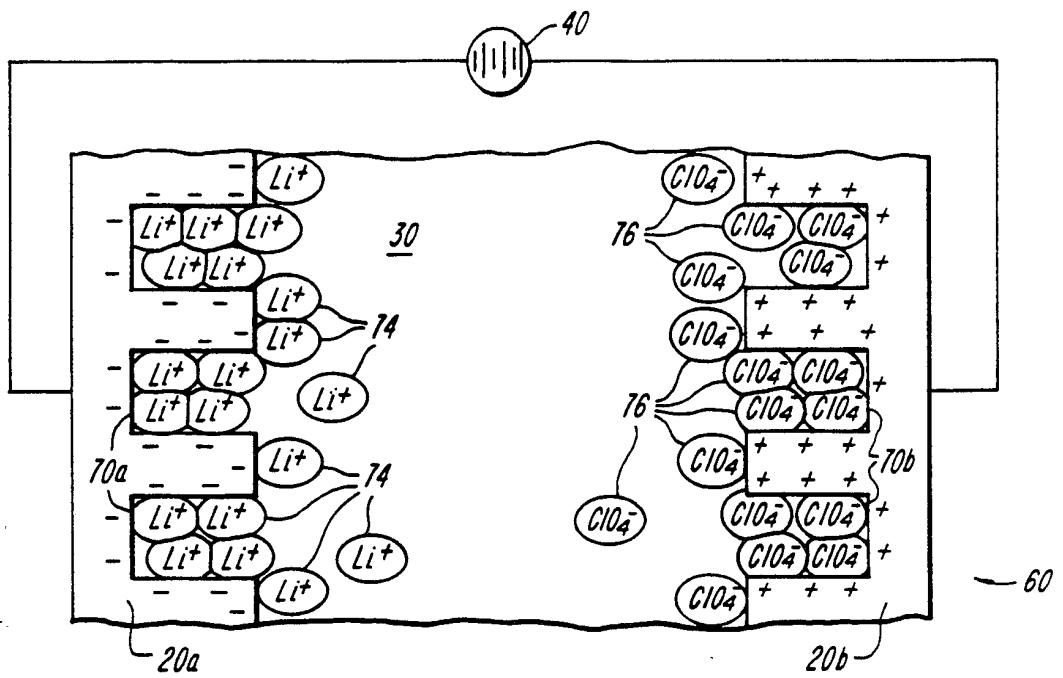
FIG. 2C

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: H01L 35/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE, A1, 3942553 (ASEA BROWN BOVERI AG), 27 June 1991 (27.06.91), abstract, see the figure.	1-32
A	EP, A2, 0227467 (FORD MOTOR COMPANY LIMITED ET AL), 1 July 1987 (01.07.87), see the whole document	1-32
A	GB, A, 2113914 (ENERGY CONVERSION DEVICES INC.), 10 August 1983 (10.08.83), abstract	3

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

*	Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	
"E"	earlier document but published on or after the international filing date	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	
"P"	document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 February 1993	1 1. 03. 93
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer RUNE BENGTSSON

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT
Information on patent family members

08/01/93

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
DE-A1- 3942553	27/06/91	NONE		
EP-A2- 0227467	01/07/87	CA-A-	1276969	27/11/90
		DE-A-	3686407	17/09/92
		JP-A-	62158860	14/07/87
		US-A-	4714798	22/12/87
GB-A- 2113914	10/08/83	AU-A-	1036583	28/07/83
		CA-A-	1185781	23/04/85
		DE-A-	3301155	28/07/83
		FR-A-	2520559	29/07/83
		JP-A-	58180076	21/10/83
		NL-A-	8300168	16/08/83
		US-A-	4447277	08/05/84