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(54) Title: A METHOD OF GENERATING THERMAL ENERGY

(57) Abstract: The present invention relates to a method of generating thermal energy, the method comprising: (i) contacting a surface of a metal with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon; and (ii) exposing the surface having hydrogen absorbed thereon to an atmosphere comprising oxygen, wherein the oxygen reacts with the absorbed hydrogen to produce thermal energy, wherein before performing step (ii) the surface is activated with an atmosphere comprising water.

WO 2012/052763 A1

A METHOD OF GENERATING THERMAL ENERGY

The present invention relates to a method of generating thermal energy and an energy storage apparatus. The present invention also relates to the use of a metal having hydrogen absorbed thereon to generate thermal energy.

Methods of generating thermal energy are of use in many different industries. Particularly of use are methods of storing potential thermal energy which may be released at an appropriate time. It is also of use to be able to recharge the energy source, so that more thermal energy can be generated.

WO2009/040539 describes a method of activating compositions comprising transition metals selected from at least one of gold, nickel, copper, ruthenium, molybdenum and platinum. In this document it is described that heat may be generated by the physical and chemical interactions of solid surfaces with gases. The heat evolution may be measured using flow-through microcalorimetry. A flow-through microcalorimeter may be used to measure the uptake of gases, heat evolution, the sorption of gases and their displacement with carrier gases at a range of temperatures and pressures.

Previously the inventors have found that heat is produced when a metal having hydrogen absorbed thereon is reacted with a pulse of oxygen. The present inventor has surprisingly found that much more thermal energy may be generated by modifying the surfaces of the metal.

It would be advantageous if at least preferred embodiments of the present invention were to overcome at least some of the disadvantages of the prior art or to provide a commercially useful alternative thereto.

It would be advantageous if at least preferred embodiments of the present invention were to provide an effective, efficient and/or environmentally friendly method of generating thermal heat, preferably using low cost materials. It would further be advantageous if at least preferred embodiments of the present invention were to provide a rechargeable method of generating thermal energy.

In a first aspect of the present invention there is provided a method of generating thermal energy, the method comprising:

(i) contacting a surface of a metal with an atmosphere comprising hydrogen and/or a hydrogen source to form a surface having hydrogen absorbed thereon; and

(ii) exposing the surface having hydrogen absorbed thereon to an atmosphere comprising oxygen and/or an oxygen source, wherein the oxygen reacts with the absorbed hydrogen to produce thermal energy,

wherein before performing step (ii) the surface is activated with an atmosphere comprising water.

In another aspect of the present invention there is provided the use of a metal having hydrogen absorbed thereon to generate thermal energy by exposing the metal having hydrogen absorbed thereon to an atmosphere comprising oxygen and/or an oxygen source, optionally after the surface has been activated with an atmosphere comprising water.

In a further aspect of the present invention there is provided an energy storage apparatus comprising:

a vessel containing metal;

a means for contacting the metal with an atmosphere comprising hydrogen to absorb hydrogen onto the surface of the metal;

a means for exposing the metal having hydrogen absorbed thereon to an atmosphere comprising water; and

a means for exposing the metal to an atmosphere comprising oxygen.

In a further aspect of the present invention there is provided a method of generating thermal energy, the method comprising:

(i) contacting a surface comprising (a) palladium or (b) cobalt and iron with an atmosphere comprising hydrogen and/or a hydrogen source to form a surface having hydrogen absorbed thereon; and

(ii) exposing the surface having hydrogen absorbed thereon to an atmosphere comprising oxygen and/or an oxygen source, wherein the oxygen reacts with the absorbed hydrogen to produce thermal energy.

Each aspect as defined herein may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

As used herein the term "generating thermal energy" includes generating heat.

The present inventor has surprisingly found that if the surface of a metal is activated with water either before, simultaneously or after (preferably before or after) it is contacted with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon then when the metal is subsequently exposed to an atmosphere comprising oxygen and/or an oxygen source, the heat generated by the reaction of the oxygen and/or oxygen source with the absorbed hydrogen is significantly more than if the metal is not treated or activated with water. This result is surprising, since typically, when looking to activate metal surfaces water is avoided. For example WO2009/040539 teaches that "in one embodiment of the present invention, preferably prior to activation of the composition, the composition is exposed to a vacuum. Treatment of the composition in this way has the advantage that unwanted water and gaseous impurities are removed from the composition prior to activation. In another embodiment of WO2009/040539, the composition is exposed to an atmosphere comprising nitrogen prior to activation". Thus, this document teaches away from exposing the composition to water, and indeed that water is unwanted.

The high heats generated by the interactions of oxygen atoms with the adsorbed hydrogen occur only as long as the adsorbed hydrogen is available and not totally consumed by the interactions. However, readsorption of the hydrogen restores the capacity of the metal, for example gold and palladium, to produce these exceptionally high generations of heat. This process is therefore reversible. It is evident that the hydrogen atoms chemisorbed on the metal display extraordinary ability to dissociate oxygen molecules, a highly endothermic process, and then produce exceptionally high heats of the interaction with the oxygen atoms. It seems therefore that at least a part of the chemisorbed hydrogen atoms is in a state of very high potential energy, but the nature of these energetic atoms remains unknown. However, the abnormally high heat evolutions described herein offer considerable opportunity for the development of novel sources of energy.

It will be understood that the term absorption as used herein does not preclude adsorption of gases on to the surface of the metal.

Preferably the metal used in the present invention is a transition metal. The metal may be an alloy of the metal. Preferably the metal is selected from one or more of gold, nickel, copper, ruthenium, molybdenum, tungsten, cobalt, silver, platinum, iron, palladium and mixtures of one or more thereof. More preferably the metal is palladium or gold. Most preferably still, the metal is palladium.

The metal is preferably in the form of powders, particles, fibres, flakes or sponges and may be deposited on a support. Suitable supports include TiO_2, silica, graphite or iron oxides. The metal preferably has a purity of at least 99% and most preferably a purity of at least 99.99%. The purity of the metal may be measured using atomic spectroscopy.

The metals used in the method described may comprise absorbed oxygen. At least some of this oxygen may be removed or at least partially removed during exposure of the metal to hydrogen. Exposure to hydrogen may at least partially reduce the oxides, but preferably some hydrogen is absorbed by the reduced metal atoms or on the unreduced metal oxide groups in the form of chemisorbed atoms.

In step (i) the surface of the metal is exposed to an atmosphere comprising hydrogen and/or hydrogen source to form a surface having hydrogen absorbed thereon. Advantageously, for some metals, such as palladium, hydrogen can be absorbed onto the surface of the metal at room temperature, advantageously for example at a temperature in the range of from 10 to 30 °C. It may also be carried out at temperatures from 10 to 130 °C. It may be preferable for the hydrogen absorption at to be carried out at an elevated temperature. For example, when the metal is or comprises gold, preferably hydrogen absorption is carried out at from 20 to 130°C. When the metal is or comprises nickel, preferably hydrogen absorption is carried out at from 150 to 250°C. When the metal is of comprises copper, preferably hydrogen absorption is carried out at from 120 to 180 °C. When the metal is or comprises ruthenium, preferably hydrogen absorption is carried out at from 50 to 200 °C. When the metal is or comprises molybdenum, preferably hydrogen absorption is carried out at from 150 to 250°C. When the metal is or comprises tungsten, preferably hydrogen absorption is carried out at from 150 to 250°C. When the metal is or comprises cobalt, preferably hydrogen absorption is carried out at from 150 to 250°C. When the metal is or comprises silver, preferably hydrogen absorption is carried out at from 150 to 250°C. When the metal is or comprises platinum, preferably hydrogen absorption is carried out at from 50 to 150°C. When the metal is or comprises iron, preferably hydrogen absorption is carried out at from 150 to 250°C. When the metal is or comprises palladium, preferably hydrogen absorption is carried out at from 10 to 130°C.

Preferably, the surface of the metal is exposed to an atmosphere comprising from 0.1 % to 100% vol of hydrogen, optionally mixed with an inert gas, to preferably obtain a chemisorbed hydrogen content per gram of metal, from 5 to 100 μmol. More preferably, the surface of the metal is exposed to atmosphere comprising from 80 % vol to 100 % vol of hydrogen, optionally mixed with an inert gas, to obtain a hydrogen content of the metal ranging from 5 to 50 μmol per gram of the metal.

Preferably, after step (i) the absorbed, preferably chemisorbed, hydrogen content per gram of metal is from 5 to 100 μmol. More preferably after step (i) the absorbed, preferably chemisorbed, hydrogen content is from 5 to 50 μmol per gram of the metal.

Preferably, in step (i) the surface is exposed to an atmosphere comprising from 0.5 to 150 μmol of hydrogen per 0.1 to 500 m^2/g specific surface area of the metal.
More preferably, in step (i) the surface is exposed to an atmosphere comprising from 1 to 100 μmol of hydrogen per 0.1 to 500 m^2/g specific surface area of the metal.

In one embodiment, in step (i) the surface of the metal is exposed to an atmosphere comprising hydrogen and/or a hydrogen source to form a surface which contains chemisorbed hydrogen atoms.

As used herein the term "a surface of a metal having hydrogen absorbed thereon" preferably means that the surface of the metal has hydrogen atoms chemisorbed thereon. Preferably, such a surface is capable of producing intense heat evolution on contact with molecular oxygen. For example from 0.1g to 1.0 g of a metal powder containing at least 10 micromoles of chemisorbed hydrogen atoms will interact with approximately 0.5 micromoles of molecular oxygen to produce at least 300 $kJmol^{-1}$ of heat, and preferably at least 500 $kJmol^{-1}$.

Preferably, prior to exposing the surface of a metal to an atmosphere comprising hydrogen and/or a hydrogen source to absorb hydrogen thereon, the surface of the metal is purged with an inert gas, preferably at approximately 120°C. In this way, gaseous and other impurities present on the surface of the metal may be removed. Prior to exposure of the surface of the metal with an atmosphere comprising hydrogen and/or a hydrogen source, it may be exposed to an atmosphere comprising nitrogen and/or a noble gas. The noble gas may be selected from argon, neon, helium, or a mixture of two or more thereof. More preferably the noble gas comprises one of at least argon and neon. Most preferably the noble gas comprises argon.

Absorption of hydrogen onto the surface of a metal may be measured by a thermal conductivity detector which senses and determines the amount of hydrogen in the effluent emerging from the FMC (Flow-through Microcalorimetry) containing the metal sorbent. Such detectors are know in the art, for example those described in Kung, H.H *et al*, Journal of Physical Chemistry B 2005, 109, 5498-5502.

The present inventor has seen the largest increases in heat generation when prior to step (ii) (exposing the surface having hydrogen absorbed thereon to an atmosphere comprising oxygen and/or an oxygen source) at least some of the hydrogen which is absorbed onto the surface of the metal is desorbed. Without wishing to be bound by theory, it is thought that this allows regulation and a substantially even distribution of the strongly absorbed hydrogen atoms on the surface of the metal. Therefore, preferably, after step (i) and before step (ii) at least a portion of the hydrogen which is absorbed on the surface of the metal is desorbed. Desorbing at least a portion of the absorbed hydrogen may be achieved by flowing an inert gas or nitrogen over the surface having hydrogen absorbed thereon. Preferably nitrogen gas is used to desorb at least a portion of the absorbed hydrogen from the surface of the metal. Preferably at least 50%, at least 70%, at least 80% or at least 90% of the initially absorbed hydrogen is desorbed from the metal before step (ii) is carried out based on the total amount of hydrogen absorbed in the metal. After the desorption step preferably, at least 50%, at least 30%, at least 10% or at least 5% of the hydrogen which is absorbed in the metal remains absorbed in the metal based on the total amount of hydrogen absorbed in the metal.

In one embodiment 95% of the originally absorbed hydrogen is desorbed from the surface prior exposure of the surface to oxygen.

Preferably either after step (i) or after step (i) followed by a desorbtion step, the surface of the metal is from 0.1% to 20% saturated with absorbed hydrogen. The saturation of the surface with absorbed hydrogen is measured by determining the desorbed hydrogen with a thermal conductivity detector. More, preferably either after step (i) or after step (i) followed by a desorbtion step, the surface of the metal is from 0.1% to 10% saturated with the absorbed hydrogen.

Before performing step (ii) the surface of the metal is activated with an atmosphere comprising water. The surface may be activated by exposing it to an atmosphere comprising water before, or after the surface is contacted with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon. Preferably, the surface is activated by exposing it to an atmosphere comprising water before or after the surface is contacted with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon. More preferably still, the surface is activated by exposing it to an atmosphere comprising water after the surface is contacted with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon.

The atmosphere comprising water may, for example, comprise wet hydrogen gas, or a wet carrier gas.

Preferably, the surface of the metal is exposed to an atmosphere comprising from 0.01 µmol to 100 µmol of water per gram of metal, from 0.01 to 80 µmol, from 0.01 to 10 µmol, from 0.1 to 5 µmol, or from 0.1 to 2 µmol of water per gram of metal. More preferably, the surface of the metal is exposed to atmosphere comprising from 1 to 10 µmol of water per gram of metal.

The present inventor has found that if low levels of water are used in the activation step (for example, less than 0.01 µmol of water per gram of metal) then the level of increase in generation of thermal energy upon exposure to oxygen compared to when the metal is not exposed to water is small.

The present inventor has also found that if high levels of water are used in the activation step (for example, greater than 100 µmol, or greater than 150 µmol, of water per gram of metal then the metal may be deactivated, it is thought that at such high levels the water prevents or reduces the interaction of the absorbed hydrogen with the oxygen and/or oxygen source.

Preferably, the surface of the metal is exposed to water which is not generated by reaction of hydrogen and oxygen on the surface of the metal. Instead, preferably, "fresh", new water is added to the system. The water is actively added to the system, it is not present as a result of a reaction.

Preferably, the surface, preferably having hydrogen absorbed thereon, is exposed to an atmosphere comprising from 1 to 500 µmol of water per 1 to 500 m^2/g specific surface area of the metal. More preferably, the surface, preferably having hydrogen absorbed thereon, is exposed to an atmosphere comprising from 1 to 200 µmol of water per 1 to 200 m^2/g specific surface area of the metal.

The oxygen source may be pure oxygen (oxygen gas having a purity of at least 95%, at least 99%, at least 99.99%), air, oxygen in an inert gas, or mixtures of one or more thereof. The oxygen source may for example be or comprise hydrogen peroxide and/or ozone.

The surface having hydrogen absorbed thereon may be exposed to an atmosphere comprising one or more noble gases. The noble gas may be selected from argon, neon, helium, or a mixture of two or more thereof. More preferably the noble gas comprises one of at least argon and neon. Most preferably the noble gas comprises argon.

In step (ii) the surface of the metal having hydrogen absorbed thereon is exposed to an atmosphere comprising oxygen and/or an oxygen source wherein the oxygen reacts with the absorbed hydrogen to produce thermal energy.

Preferably, the reaction is carried out under conditions such that water is not formed by the reaction of the oxygen and/or oxygen source with the absorbed hydrogen. For metal particles deposited on microporous solids having high surface areas relatively higher additions of water vapour may be tolerated.

Preferably, in step (ii) the surface having hydrogen absorbed thereon is exposed to an atmosphere comprising 0.05 to 100 µmol of oxygen per gram of metal. More preferably, in step (ii) the surface having hydrogen absorbed thereon is exposed to an atmosphere comprising from 0.1 to 50 µmol of oxygen per gram of metal, from 1 to 50 µmol of oxygen per gram of metal, or from 0.05 to 10 μmol of oxygen per gram of metal.

Preferably, in step (ii) the surface having hydrogen absorbed thereon is exposed to an atmosphere comprising from 0.05 to 200 μmol of oxygen per 0.1 to 300 m^2/g specific surface area of the metal. More preferably, in step (ii) the surface having hydrogen absorbed thereon is exposed to an atmosphere comprising from 0.1 to 100 μmol of oxygen per 1 to 100 m^2/g specific surface area of the metal.

The specific surface area of the metal may be measured by any suitable known technique, for example by a BET adsorption method.

It will be understood that the oxygen may be provided as gaseous oxygen, or a source of oxygen, such as hydrogen peroxide. The source of oxygen may be non-gaseous.

The present inventor has found that if the surface having hydrogen absorbed thereon is exposed to an atmosphere comprising less than 0.05 μmol of oxygen per gram of metal then the significant thermal energy (or heat) is typically not generated.

If the surface of a metal powder is exposed to an atmosphere consisting of 100 % pure hydrogen resulting in full saturation of the metal with hydrogen and the weakly adsorbed hydrogen is not desorbed by an inert gas then the present inventor has surprisingly found that typically large heat evolutions are not observed. Without wishing to be bound to any particular theory it is thought that exposure of the surface having hydrogen absorbed thereon to excessive amounts of oxygen tends to produce water which is associated with low heat evolution. It is thought that evolution of high heats (for example, two, three, four, five or more times the heat of water formation) is not accompanied by the formation of water and appears to be related to the reaction (s) between the chemisorbed hydrogen and dissociated oxygen atoms.

The surface having hydrogen absorbed thereon may be exposed to a pulse of oxygen and/or a source of oxygen.

As used herein the term "pulse" is used to describe exposing a composition to a specified gas for a short period of time, typically seconds, or minutes. The length of exposure will depend on the desired amount of gas that is to be exposed to the composition and, for example, the flow rate of the gas etc. A pulse as used herein is not a meant to describe a continuous or extended period of exposure of a gas to the composition.

A continuous flow of an atmosphere comprising oxygen, for example oxygen diluted in an inert carrier gas may be used. However, in this case, preferably the amount of oxygen does not exceed the limits stated above.

The surface having hydrogen absorbed thereon may be exposed to repeated pulses of oxygen and/or sources of oxygen. The present inventor have found that by exposing the surface to repeated pulses of oxygen and/or sources of oxygen, large heat effects are seen after several pulses, until little or no heat effect is observed after further additions of pulses of oxygen and/or sources of oxygen. Without wishing to be bound by any particular theory, it is thought that heat effects are observed until all, or almost all of the hydrogen absorbed on the surface has been consumed.

After the surface having hydrogen absorbed thereon has been exposed to an atmosphere comprising oxygen and/or a source of oxygen, and preferably after at least some, and preferably all of the absorbed hydrogen has been consumed, the surface may be recharged by contacting it with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon. Thus, the surface may be "recharged" with absorbed hydrogen and the process may be repeated.

The method may be performed as a continuous process for the generation of thermal energy by repeating steps (i) and (ii) in turn.

In one aspect there is provided a method of generating thermal energy, the method comprising:

(i) contacting a surface comprising (a) palladium or (b) cobalt and iron with an atmosphere comprising hydrogen and/or a hydrogen source to form a surface having hydrogen absorbed thereon; and

(ii) exposing the surface having hydrogen absorbed thereon to an atmosphere comprising oxygen and/or an oxygen source, wherein the oxygen reacts with the absorbed hydrogen to produce thermal energy.

In this aspect, the present inventors have found that large amounts of thermal heat may be generated even in the absence of an activating water step.

Palladium is known to absorb hydrogen at ambient temperatures and atmospheric pressures. The absorption of hydrogen is exothermic and it is generally accepted that it occurs after dissociation of hydrogen molecules into atoms. This process may take place during the exposure of palladium immersed in different inert atmospheres, such as nitrogen, helium and argon even when the partial pressure of hydrogen in the gas mixtures falls to very low values. The preferential adsorption of hydrogen is very rapid at room temperatures, producing sharp evolution of heat. Desorption of the absorbed hydrogen with a flow of nitrogen is relatively slow at room temperatures, about 8000 volumes of nitrogen flow being required to completely desorb hydrogen at atmospheric pressures from 1 volume of a palladium powder at room temperatures. The desorption times may be longer for fine powders and supported Pd particles, the rates of desorption being indicated by the shape of the heat endotherms. Generally, the rates of desorption are relatively low allowing introduction of pulses of reactants, such as oxygen, into the flow of carrier gas, which then interact with the absorbed hydrogen.

The present inventor has surprisingly found that exceptionally high heat evolutions are observed when the surface comprises cobalt and iron. The inventor has found that if the surface comprises only one of cobalt or iron, the exceptionally high heat evolutions are not observed. Accordingly, the combination of cobalt and iron results in an advantageous synergistic effect. Preferably, the surface comprises from 0.1 to 5 wt %, more preferably 0.5 to 2.5 wt %, more preferably still 0.8 to 1.5 wt %, most preferably 1 wt % cobalt relative to the amount of iron. If the surface comprises more than 5 wt % cobalt, no additional effect is observed relative to the effect observed when the surface comprises 1 wt % cobalt relative to the amount of iron. Accordingly, it is preferable that the amount of cobalt be as low as possible since cobalt is expensive.

It is assumed that the oxygen molecules contacting the adsorbed hydrogen atoms undergo dissociation into atoms and then rapidly interact with the adsorbed or absorbed hydrogen, generating heat evolutions which greatly exceed the heat of formation of water from molecular H_2 and O_2. The evolution of heat may be affected by helium and argon accompanying oxygen interacting with the hydrogen absorbed by palladium.

The inventors have found that the small size of gold particles supported on TiO_2 leads to a marked increase in the generation of heat produced by the reaction with oxygen. This may also be partly caused by an activating effect of the supporting TiO_2. For palladium particles supported on an active carbon this effect was detected at temperatures exceeding 100 °C. On the other hand, the heat generation by the interaction of oxygen with pure Pd powder at 25°C is markedly greater than the heat generated at 125°C. For gold, conversely, the interaction with oxygen at 125°C produces much more heat than that determined at room temperatures.

The palladium may be an alloy. Palladium may be present in combination with one or more of gold, nickel, copper, ruthenium, molybdenum, tungsten, cobalt, silver, platinum, iron. The palladium is preferably in the form of powders, particles, fibres, flakes or sponges and may be deposited on a support.

The cobalt and iron may be an alloy or alloys. Cobalt and iron may be present in combination with one or more of gold, nickel, copper, ruthenium, molybdenum, tungsten, silver, platinum, palladium. The cobalt and iron are preferably each in the form of powders, particles, fibres, flakes or sponges or mixtures thereof, or each deposited on a support. Preferably, the cobalt is deposited on the iron. Preferably, the iron is in the form of flakes. Most preferably, the cobalt and iron is an alloy.

A 1 wt% cobalt/iron alloy may be produced by co-grinding cobalt and iron powders in a Vibratory Ball Mill or by other conventional techniques. Similar alloys can be produced by, for example, co-grinding palladium and iron and nickel and iron.

The palladium or cobalt and iron may be deposited on a support, such as TiO_2, silica, graphite or iron oxide. The palladium or cobalt and iron respectively preferably have a purity of at least 99% and most preferably a purity of at least 99.99%. The purity of the respective metals may be measured using atomic spectroscopy.

In step (i) the surface of the palladium or cobalt and iron is exposed to an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon. As outlined above, advantageously for palladium, hydrogen can be absorbed onto the surface of the palladium at room temperature, for example at a temperature in the range of from 10 to 30°C. The reaction may also be carried out at temperatures in the range of from 10 to 130°C.

The reaction wherein the surface comprises cobalt and iron may be carried out at from 180°C to 220°C, preferably at from 190°C to 210°C, more preferably at from 195°C to 205°C.

Preferably, the surface is exposed to atmosphere comprising from 1 to 100 µmol of hydrogen per gram of palladium or molar equivalent of cobalt and iron, from 10 to 50 µmol of hydrogen per gram of palladium or molar equivalent of cobalt and iron, from 50 to 100 µmol, or from 1 to 10 µmol of hydrogen per gram of palladium or molar equivalent of cobalt and iron. More preferably, the surface is exposed to an atmosphere comprising from 5 to 50 µmol of hydrogen per gram of palladium or molar equivalent of cobalt and iron.

Preferably, the surface is exposed to an atmosphere comprising from 0.5 to 150 µmol of hydrogen per 0.1 to 500 m^2/g specific surface area of the palladium or molar equivalent of cobalt and iron. More preferably, the surface is exposed to an atmosphere comprising from 1 to 100 µmol of hydrogen per 0.1 to 500 m^2/g specific surface area of the palladium or molar equivalent of cobalt and iron.

In one embodiment, in step (i) the surface is exposed to an atmosphere comprising hydrogen to form a surface which is saturated with hydrogen absorbed thereon.

Preferably, prior to exposing the surface of to an atmosphere comprising hydrogen to absorb hydrogen thereon, the surface is purged by an inert carrier gas, preferably at approximately 120°C. In this way, gaseous and other impurities present on the surface of the metal may be removed. Prior to exposure of the surface with an atmosphere comprising hydrogen, it may be exposed to an atmosphere comprising nitrogen and/or a noble gas. The noble gas may be selected from argon, neon, helium, or a mixture of two or more thereof. More preferably the noble gas comprises one of at least argon and neon. Most preferably the noble gas comprises argon.

The present inventors have seen the largest increases in heat generation when prior to step (ii) (exposing the surface having hydrogen absorbed thereon to an atmosphere comprising oxygen) at least some of the hydrogen which is absorbed onto the surface is desorbed. Therefore, preferably, after step (i) and before step (ii) at least a portion of the hydrogen which is absorbed on the surface is desorbed. Desorbing at least a portion of the absorbed hydrogen may be achieved by flowing an inert gas over the surface having hydrogen absorbed thereon.

Preferably either after step (i) or after step (i) followed by a desorbtion step, the surface is from 0.1% to 20% saturated with absorbed hydrogen. More, preferably either after step (i) or after step (i) followed by a desorbtion step, the surface of the metal is from 0.1% to 10% saturated with absorbed hydrogen.

Preferably, before performing step (ii) the surface is activated with an atmosphere comprising water. The surface may be activated by exposing it to an atmosphere comprising water before, or after the surface is contacted with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon. Preferably, the surface is activated by exposing it to an atmosphere comprising water before or after the surface is contacted with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon. More preferably still, the surface is activated by exposing it to an atmosphere comprising water after the surface is contacted with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon.

Preferably, the surface is exposed to an atmosphere comprising from 0.01 to 10000 µmol of water per gram of palladium or molar equivalent of cobalt and iron, from 0.1 to 5000 µmol of water per gram of palladium or molar equivalent of cobalt and iron, or from 0.1 to 2000 µmol of water per gram of palladium or molar equivalent of cobalt and iron. More preferably, the surface is exposed to atmosphere comprising from 1 to 1000 µmol of water per gram of palladium or molar equivalent of cobalt and iron.

Preferably, the palladium or cobalt and iron, preferably having hydrogen absorbed thereon, is exposed to an atmosphere comprising from 1 to 500 µmol of water per 1 to 500 m^2/g specific surface area of the palladium or molar equivalent of cobalt and iron. More preferably, the palladium or cobalt and iron, preferably, having hydrogen absorbed thereon is exposed to an atmosphere comprising from 1 to 200 µmol of water per 1 to 200 m^2/g specific surface area of the palladium or molar equivalent of cobalt and iron.

Preferably, the surface is exposed to water which is not generated by reaction of hydrogen and oxygen on the surface. Instead, preferably, “fresh”, new oxygen is added to the system.

The oxygen source may be pure oxygen (oxygen gas having a purity of at least 95%, at least 99%, at least 99.99%), air, oxygen in an inert gas, or mixtures of one or more thereof. The oxygen source may for example be or comprise hydrogen peroxide and/or ozone.

The surface having hydrogen absorbed thereon may be exposed to an atmosphere comprising one or more noble gases. The noble gas may be selected from argon, neon, helium, or a mixture of two or more thereof. More preferably the noble gas comprises one of at least argon and neon. Most preferably the noble gas comprises argon.

The present inventor has surprisingly found that if argon is used as a carrier gas for the pulse of oxygen much larger amounts of heat are generated.

In step (ii) the surface of the metal having hydrogen absorbed thereon is exposed to an atmosphere comprising oxygen wherein the oxygen reacts with the absorbed hydrogen to produce thermal energy.

Preferably, in step (ii) the surface having hydrogen absorbed thereon is exposed to an atmosphere comprising from

0.05 to 100 µmol of oxygen per gram of palladium or molar equivalent of cobalt and iron. More preferably, in step (ii) the surface having hydrogen absorbed thereon is exposed to an atmosphere comprising from 1 to 50 µmol of oxygen per gram of palladium or molar equivalent of cobalt and iron, or from 0.05 to 10 µmol of oxygen per gram of palladium or molar equivalent of cobalt and iron.

The present inventor has found that if the surface having hydrogen absorbed thereon is exposed to an atmosphere comprising less than 0.05 µmol of oxygen per gram of palladium or molar equivalent of cobalt and iron then the significant thermal energy (or heat) is typically not generated.

Preferably, the surface having hydrogen absorbed thereon is exposed to an atmosphere comprising from 0.05 to 200 µmol of oxygen per 0.1 to 300 m^2/g specific surface area of the palladium or molar equivalent of cobalt and iron. More preferably, the surface having hydrogen absorbed thereon is exposed to an atmosphere comprising from 0.1 to 100 µmol of oxygen per 1 to 100 m^2/g specific surface area of the palladium or molar equivalent of cobalt and iron.

The surface having hydrogen absorbed thereon may be exposed to a pulse of oxygen.

The surface having hydrogen absorbed thereon may be exposed to repeated pulses of oxygen. The present inventors have found that by exposing the surface to repeated pulses of oxygen, large heat effects are seen after several pulses, until little or no heat effect is observed after further additions of pulses of oxygen. Without wishing to be bound by any particular theory, it is thought that heat effects are observed until all, or almost all of the hydrogen absorbed on the surface has been used.

After the surface having hydrogen absorbed thereon has been exposed to an atmosphere comprising oxygen, and preferably after at least some, and preferably all of the absorbed hydrogen has been consumed, the surface may be recharged by contacting it with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon. Thus, the surface may be "recharged" with absorbed hydrogen and the process may be repeated.

The present invention may be carried out at pressures from atmospheric pressure (approximately 10^5 Pa/g) to 150 bar/g (1.5×10^7 Pa/g). Most preferably the pressure is between atmospheric pressure (approximately 10^5 Pa/g) and 30 bar/g (3×10^6 Pa/g).

In one aspect of the present invention there is provided the use of a metal having hydrogen absorbed thereon to generate thermal energy by exposing the metal having hydrogen absorbed thereon to an atmosphere comprising oxygen, optionally after the surface has been activated with an atmosphere comprising water.

In one aspect of the present invention there is provided an
energy storage apparatus comprising:
an energy storage apparatus comprising:
a vessel containing metal;

a means for contacting the metal with an atmosphere comprising hydrogen to absorb hydrogen onto the surface of the metal;

a means for exposing the metal having hydrogen absorbed thereon to an atmosphere comprising water; and

a means for exposing the metal to an atmosphere comprising oxygen.

As used herein the term "vessel" means a gas tight (air-tight) container, which comprises a means for introducing and releasing a specific gas, or mixture of gases, such that the atmosphere in the vessel may be controlled.

The present invention is described by way of example in relation to the following figures.

Figure 1: shows the heats of adsorption of hydrogen and oxygen on 5% Pd on active Carbon at 123°C.

Figure 2: shows the adsorption of H_2, a pulse of H_2O and 0.45 µmol O_2 in Argon

Figure 3: shows the heats of exposure of a 0.259 g sample of palladium powder to oxygen after reduction with hydrogen at 25°C. Comparison of the heats of adsorption of equal amounts of pure oxygen and the oxygen mixed with argon.

Figure 4: shows heats of adsorption of oxygen on 0.327g of palladium with oxygen at 125°C.

Figure 5: shows heats of exposure of a 0.053 g of palladium catalyst supported on an active carbon at 25°C. The

palladium was exposed to two times 0.45µmol of oxygen in argon.

Figure 6: shows heats of exposure of a 0.53 g sample of palladium catalyst supported on an active carbon at 125°C. The sample was exposed to 2 µmol pulses of pure oxygen.

Examples:

The present invention will now be described further, by way of example only, with reference to the following Examples.

Equipment: The surface energy measurements were carried out using a Microscal Flow-trough Microcalorimeter as described in Chemistry and Industry 25th March 1965, pages 482 to 489 and Thermochimica Acta, 312, 1998, pages 133 to 143.

In the experiments described the tubes were extensively purged with the gases under examination to remove the oxygen adsorbed on the walls of the tubes.

The adsorption experiments described herein were conducted by exchanging the flow of nitrogen for those of pure hydrogen, oxygen, noble gas or the gas under investigation. The resulting exposures of the metals to the gases were maintained for seconds or minutes for the pulse experiments, or hours to achieve complete saturation, i.e. until no further uptake of the interacting gases was recorded by the thermal conductivity detector. The pulses were separated by nitrogen flows long enough to remove any oxygen or noble gas that was not retained (absorbed) by the metal powders.

In order to ensure that the pulses of the gases passing through stainless steel capillaries are free from any impurities, especially any adsorbed oxygen on the internal walls of the steel tubing, purification of the internal walls of the tubing was carried out in each case, before the exchanges, for example, by passing at least 100 cc of each gas through the tubing before their exchanges with nitrogen flows.

The abnormally high heat generated in this method can reach, for example five to twelve times higher than the heats of formation of gaseous water from molecular hydrogen and oxygen, which offers the development of new sources of energy for domestic and industrial purposes.

Example 1

An 0.251g sample of palladium powder was exposed to an atmosphere comprising hydrogen to provide palladium containing chemisorbed hydrogen at 25°C. The palladium powder was then exposed to 0.45µmol of oxygen in an argon carrier gas. This resulted in 1706mJ of heat being evolved, which equates to 3791kJ/mol of heat per mol of oxygen.

The sample of palladium was then exposed to a further 0.45µmol of oxygen in an argon carrier gas. This time 1488mJ of heat were evolved, which equates to 3306kJ/mol of heat per mol of oxygen.

The sample of palladium was then exposed to a further 0.45µmol of oxygen in an argon carrier gas. This resulted in 1413mJ of heat being evolved, which equates to 3140kJ/mol of heat per mol of oxygen.

The sample of palladium was then exposed to a further 0.45µmol of oxygen in a nitrogen carrier gas. This resulted in 618mJ of heat being evolved, which equates to 1373kJ/mol of heat per mol of oxygen.

The sample of palladium was then exposed to a further 0.45µmol of oxygen in a nitrogen carrier gas. This resulted in 658mJ of heat being evolved, which equates to 1456kJ/mol of heat per mol of oxygen.

The sample of palladium was then exposed to a further 0.45µmol of oxygen in a nitrogen carrier gas. This resulted in 668mJ of heat being evolved, which equates to 1489kJ/mol of heat per mol of oxygen.

Example 2

An 0.251g sample of palladium powder was exposed to an atmosphere comprising hydrogen to provide palladium containing chemisorbed hydrogen at 25°C. The palladium powder was then exposed to 0.45µmol of oxygen in a helium carrier gas. This resulted in 606mJ of heat being evolved, which equates to 1347kJ/mol of heat per mol of oxygen.

The sample of palladium was then exposed to a further 0.45µmol of oxygen in a helium carrier gas. This resulted in 619mJ of heat being evolved, which equates to 1376kJ/mol of heat per mol of oxygen.

The sample of palladium was then exposed to a further 0.45μmol of oxygen in a helium carrier gas. This resulted in 544mJ of heat being evolved, which equates to 1209kJ/mol of heat per mol of oxygen.

Example 3

An 0.251g sample of palladium powder was exposed to an atmosphere comprising hydrogen to provide palladium containing chemisorbed hydrogen at 25°C. The palladium powder was then exposed to 0.45μmol of oxygen in a nitrogen carrier gas. This resulted in 666mJ of heat being evolved, which equates to 1480kJ/mol of heat per mol of oxygen.

The sample of palladium was then exposed to a further 0.45μmol of oxygen in a nitrogen carrier gas. This resulted in 675mJ of heat being evolved, which equates to 1500kJ/mol of heat per mol of oxygen.

The sample of palladium was then exposed to a further 0.45μmol of oxygen in a nitrogen carrier gas. This resulted in 630mJ of heat being evolved, which equates to 1400kJ/mol of heat per mol of oxygen.

Example 4

Figure 1 shows the results of the following experiment. Heat evolution at 123 C of a 10 micromole pulse of hydrogen and 0.45 micromole pulse of oxygen mixed with argon (1 cc of 1% vol of oxygen in argon) on 53 mg of Pd/carbon sample containing 5% wt of Pd. The heat of adsorption of oxygen follows that produced by the hydrogen pulse and its partial desorption by the nitrogen carrier gas before its interaction with 0.45 µmol of oxygen generating heat evolution of 1428 mJ equivalent to 3173 kJ/mol/ O_2 . This heat evolution exceeds that of the formation of water from molecular hydrogen and oxygen by a factor of 6.6.The high heat evolution was obtained after the Pd particles deposited on an activated carbon were exposed to 5 µmol pulse of water before the interactions with hydrogen and oxygen. The water pulse was almost completely absorbed and is not visible in the figure.

Example 5

Figure 2 shows the results of the following experiment. Heat evolutions produced by the interactions of 10 micromoles of hydrogen 5 µmol of water vapour and 0.45 micromole of oxygen mixed with argon on 0.259g of unsupported Pd powder at 25 C. The absorption of hydrogen produces a heat evolution of 637 mJ following a 600 mJ *in situ* calibration peak. The subsequent flow of nitrogen desorbing 3.3 micromole of the absorbed hydrogen is followed by a 5 µmol pulse of water vapour producing a 2 mJ heat effect to small to be visible in the figure. A 0.45 micromole pulse of oxygen followed generating heat evolution of 2632 mJ equivalent to a molar heat of absorption of 5849 kJ/mol/O_2. This heat evolution exceeded the heat of formation of water from molecular hydrogen and oxygen by a factor of 12.1

Example 6

This example shows the heats of interaction of molecular oxygen (0.45 micromoles) with 0.259 g of palladium powder after their reduction with hydrogen at 25°C.

Pd sample,g	Treatment	Heat of interaction	Molar heat	Increase over heat
		with oxygen, mJ	kJ/mol of O_2	of water formation
0.040/sand mix	red.H_2	614	1364	x 2.8
0.259	red.H_2	580	1289	x 2.7
0.259	red.H_2, 5 µmol H_2O	2632	5849	**x 12.1**
	red. H_2	591	1314	**X 2.7**
0.259	repeat N_2 flow	226	501	x 1.0
0.259	repeat red. H_2	367	813	**X 1.7**
0.023g dep. on a.c. carbon	Red. H_2	225	500	x 1.0
0.023g repeat	N_2 flow	389	864	x 1.80
0.023g repeat	N_2 flow	406	902	x 1.89
0.023g repeat	red,H_2/ 5 µmol $H_2$0	609	1353	x 2.8

High heats of interaction of molecular oxygen with palladium are obtained when palladium contains absorbed hydrogen which is subjected to an initial stage of desorption by a flow of an inert gas, such as nitrogen. The heat evolutions become relatively low when the exposures to oxygen are increased to quantities exceeding 2 micromoles per 10 gram atoms of the absorbed hydrogen. Exposure to larger amounts of oxygen tends to produce water which is associated with relatively low heat evolution. Evolution of the high heats is not thought to be accompanied by the formation of water and appears to be related to the reaction, or reactions, between the chemisorbed hydrogen and dissociated oxygen atoms. Palladium seems to be especially effective at producing high heats with small amounts of oxygen. This may be because it is capable of absorbing more hydrogen than most of the other metals known at present and can do this at room temperatures.

An important factor increasing the heat evolutions is the pre-adsorption of water vapour by the palladium powders. (This applies also to other metals capable of adsorbing hydrogen, such as gold, nickel and iron). The effective amounts of water vapour typically range between 1 to 50 micromoles per gram of palladium powders and preferably between 1 and 10 micromoles. In this example the amount of water to which the palladium powders were exposed was 20 micromoles per gram.

The high heat generation can be obtained continuously in an arrangement in which hydrogen and oxygen (it could be air, mixtures of O_2 and inert gases, or, pure oxygen) are passed through finely divided palladium maintaining appropriate proportions of chemisorbed hydrogen, coming into contact with oxygen in a regime not producing any water.

Example 7

Heats of interaction of oxygen (0.45 micromoles) with hydrogen chemisorbed on platinum, nickel and iron particles

Run	Sample	Temperature °C	Heat of O_2 interations		Ratio of the molar heat of O_2 to that of water formation
			mJ/g	kJ/mol	
1	0.131g 1% Pt on Al_2O_3	30	880	1955	4.5
2	Repeat	30	577	1282	2.6
3	Repeat	128	1864	4142	8.6
4	Pure Ni 0.343g	179	740	1664	3.4
5	Repeat	179	869	1931	4.0
6	1%Ni/Fe 0.020 g	216	**1608**	3573	7.4
7	Pure Fe 0.300 g	216	365	811	1.7
8.	Repeat	216	359	798	1.7

The results listed in examples 7 and 8 were obtained using the same experimental procedures as those reported in examples 1 to 6, with different adsorbents and temperatures.

Example 8

Figure 3 shows the heats produced by the interaction of 0.45 µmol pulses of oxygen with the sample of palladium powder containing the absorbed hydrogen. The amount of the absorbed hydrogen constituted about 10% of the hydrogen that the Pd sample is capable of adsorbing at 25°C. At this level of H_2 adsorption, the rate of its desorption by nitrogen flow was relatively slow and the oxygen pulses interacting with the Pd sample encountered large numbers of the absorbed hydrogen atoms with which the oxygen pulses could interact. Displacement of the nitrogen carrier gas by 0.45 µmol of oxygen mixed with argon produced heat evolutions that were on average 4.7 times higher than the heats of formation of water. However, in this case, the 0.45 µmol pulses of pure oxygen generated heat evolutions which were 5.4 times higher than the heats produced by the O_2/Ar pulses. It appears therefore that, for the pulses of oxygen mixed with argon, the latter gas depresses the evolution of the heat of the interaction of pure Pd powder with oxygen. The reverse occurred for the interaction of oxygen with hydrogen adsorbed on gold in the presence of argon.

The adsorption of oxygen on the Pd powder at 125°C produced significantly lower heats than those obtained at 25°C, as shown in Figures 3 and 4. The latter figure shows the heat evolutions obtained at 123°C by the pulses of O_2 mixed with argon.

For 5% Pd supported on active carbon the interactions with oxygen were markedly affected by temperature. The results of these interactions are shown in Figures 1, 5 and 6. The heat evolutions recorded in this series produced heat evolutions that were 6.6, 3.5 and 3.0 times higher than the heats of water formation at 123 and 25°C respectively. The formation of water was not detected in any of the exposures of Pd to 0.45 µmol of pure oxygen. However the palladium powder was able to produce the abnormally high heats of adsorption with much greater amounts of oxygen than those observed for the gold particles, which had a relatively much lower capacity for the chemisorption of hydrogen.

The results shown in example 7 were obtained in the same way as those shown in examples 1 to 6. The results demonstrate that different transition metals are capable of producing similarly high heat evolutions at appropriate temperatures at which the metals can chemisorb hydrogen. An alloy of 1% of Ni and iron was especially effective in this respect producing heat evolution 7.4 higher than the heat of formation of water. This was obtained by a 0.020g metal sample in the form of high surface area metal flakes. 1% Pt deposited on Al2O3 was even more effective in this respect producing a heat evolution of 8.6 higher than the heat of water formation

Example 9

Sequential heat evolutions on 0.93g of 1% Au/TiO_2 sample at 125°C exposed to water, hydrogen and 1% oxygen in argon.

Run	Experiment	Heat Evolution, mJ	Molar Heat, kJ/mol
1	Exposure to 1 µmol water	42.7	43
2	Repeat	37.8	38
3	Exposure to hydrogen flow for 20 minutes	54,970	81
4	Exposure to 0.45 µmol of Oxygen post desorption of hydrogen	1787	3971

Comparative Example 10

Sequential heat evolution on 0.93g of 1% Au/TiO_2 sample at 125°C. No exposure to water vapour.

Run	Experiment	Heat Evolution, mJ	Molar Heat, kJ/mol
1	Exposure to hydrogen flow for 20 minutes	2,000	338
2	Exposure to 0.45 µmol of Oxygen post desorption of hydrogen	705	1,556

Example 11

Heat evolutions produced by sequential interactions of hydrogen and oxygen with 20mg 1% Cobalt/Iron catalyst at 204°C.

The 1% Cobalt/Iron catalyst is produced by co-grinding cobalt and iron powders in a Vibratory Ball Mill to produce an alloy.

	Experiment	**Heat evolution**	
	µmol	*mJ*	*kJ/mol*
1	10 H_2	516	51.6
2	0.45 pure O_2	237	526.7
3	0.45 pure O_2	292	648.9
4	0.45 pure O_2	840	1866.7
5	0.45 pure O_2	380	844.4
6	0.45 pure O_2	424	942.2
7	0.45 pure O_2	452	1004.4
8	0.45 pure O_2	484	1075.6
9	Saturation with 1000 µmol of hydrogen	33719	33.7
10	0.45 pure O_2	521	1157.8
11	0.45 pure O_2	550	1222.2
12	0.45 pure O_2	543	1206.7
13	0.45 O_2/Ar	2427	5393.3
14	0.45 O_2/Ar	2332	5182.2
15	0.45 pure O_2	430	956
16	0.45 pure O_2	452	1004.4
17	0.45 pure O_2	423	940
18	0.45 O_2/Ar	1176	2613.3
19	0.45 O_2/Ar	1524	3386.6
20	0.45 O_2/Ar	1396	1102.2
21	Saturation with 10.4 µmol O_2/Ar at 23 min	9791	941.4

All the above listed heat evolutions greatly exceed the heat of water vapour formation from molecular oxygen and hydrogen, which is 242 mJ/mol. Interactions with an amount of oxygen mixed with argon give significantly more heat evolution than the interactions with the same amount of pure oxygen.

Experiment 21 records heat evolution produced by continuous evolution of heat for 23 minutes after saturation of Co/Fe catalyst with hydrogen.

The foregoing detailed description has been provided by way of explanation and illustration and is not intended to limit the scope of the appended claims. Although preferred embodiments of the invention have been described herein in detail, it will be understood by those skilled in the art that variations may be made thereto without departing from the scope of the invention or the appended claims and their equivalents.

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

CLAIMS

1. A method of generating thermal energy, the method comprising:
   - (i) contacting a surface of a metal with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon; and
   - (ii) exposing the surface having hydrogen absorbed thereon to an atmosphere comprising oxygen, wherein the oxygen reacts with the absorbed hydrogen to produce thermal energy,

   wherein before performing step (ii) the surface is activated with an atmosphere comprising water.

2. The method of claim 1 wherein the metal is a transition metal.

3. The method of claim 1 or 2 the wherein the metal comprises one or more of gold, nickel, copper, ruthenium, molybdenum, tungsten, cobalt, silver, platinum, iron, palladium.

4. The method of claim 3 wherein the metal comprises an alloy of one or more metals.

5. The method of any one of the preceding claims wherein the metal is palladium.

6. The method of any one of the preceding claims wherein after step (i) and before step (ii) at least a portion of the hydrogen which is absorbed on the surface of the metal is desorbed.

7. The method of any one of the preceding claims wherein prior to step (ii) the surface of the metal is from 0.1% to 20% saturated with absorbed hydrogen.

8. The method of any one of the preceding claims wherein the metal is exposed to atmosphere comprising from 0.1 to 100 µmol of water per gram of metal.

9. The method of any one of the preceding claims wherein in step (ii) the surface having hydrogen absorbed thereon is exposed to an atmosphere comprising from 0.1 to 50 µmol of oxygen per gram of metal.

10. The method of any one of the preceding claims wherein in step (ii) the surface having hydrogen absorbed thereon is exposed to a pulse of oxygen.

11. The method of claim 10 wherein the surface having hydrogen absorbed thereon is exposed to repeated pulses of oxygen.

12. The method of any one of the preceding claims wherein after the surface having hydrogen absorbed thereon has been exposed to an atmosphere comprising oxygen, the surface is recharged by contacting it with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon.

13. The method of claim 12 performed as a continuous process for the generation of thermal energy by repeating steps (i) and (ii) in turn.

14. The method of any one of the preceding claims wherein the metal is in the form of a powder, particle, flake, fibre, sponge, or is deposited on a support.

15. The method of any one of the preceding claims comprising exposing the surface having hydrogen absorbed thereon to an atmosphere comprising one or more noble gases.

16. Use of a metal having hydrogen absorbed thereon to generate thermal energy by exposing the metal having hydrogen absorbed thereon to an atmosphere comprising oxygen, optionally after the surface has been activated with an atmosphere comprising water.

17. An energy storage apparatus comprising:
a vessel containing metal;
a means for contacting the metal with an atmosphere comprising hydrogen to absorb hydrogen onto the surface of the metal;
a means for exposing the metal having hydrogen absorbed thereon to an atmosphere comprising water; and
a means for exposing the metal to an atmosphere comprising oxygen.

18. A method of generating thermal energy, the method comprising:

(i) contacting a surface comprising (a) palladium or (b) cobalt and iron with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon; and

(ii) exposing the surface having hydrogen absorbed thereon to an atmosphere comprising oxygen, wherein the oxygen reacts with the absorbed hydrogen to produce thermal energy.

19. The method of claim 18, wherein the surface comprises (a) palladium.

20. The method of claim 18 or 19, wherein, after step (i) and before step (ii) at least a portion of the hydrogen which is absorbed on the surface of the metal is desorbed.

21. The method of any one of claims 18 to 20, wherein, prior to step (ii), the surface is from 0.1% to 20% saturated with absorbed hydrogen.

22. The method of any one of claims 18 to 21, wherein the surface having hydrogen absorbed thereon is exposed to an atmosphere comprising from 1 to 50 µmol of oxygen per gram of palladium or molar equivalent of cobalt and iron.

23. The method of any one of claims 18 to 22, wherein in step (ii) the surface having hydrogen absorbed thereon is exposed to a pulse of oxygen.

24. The method of claim 23, wherein the surface having hydrogen absorbed thereon is exposed to repeated pulses of oxygen.

25. The method of any one of claims 18 to 24, wherein after the surface having hydrogen absorbed thereon has been exposed to an atmosphere comprising oxygen, the surface is recharged by contacting it with an atmosphere comprising hydrogen to form a surface having hydrogen absorbed thereon.

26. A method of generating thermal energy as substantially herein described with reference to the Figures and Examples.

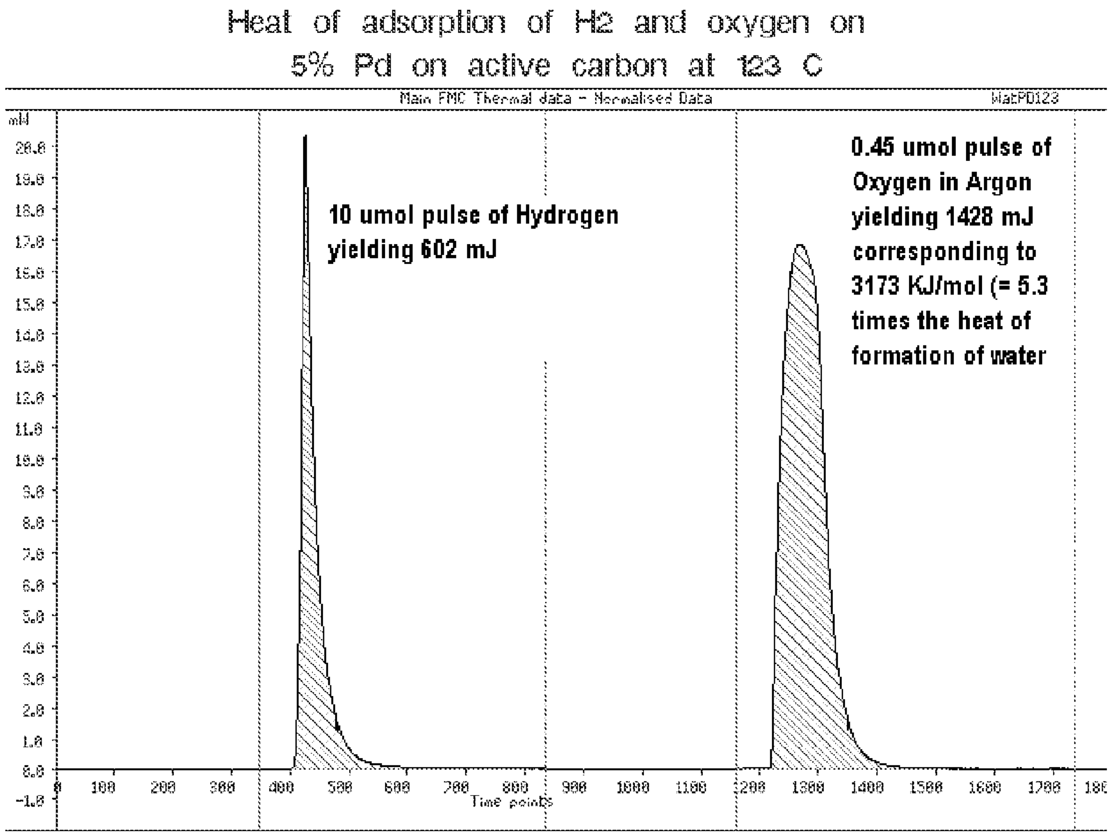
Heat of adsorption of H2 and oxygen on
5% Pd on active carbon at 123 C
Main FMC Thermal data - Normalised Data
WatPD123
mW
20.0
19.0
18.0
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
Time points
10 umol pulse of Hydrogen
yielding 602 mJ
0.45 umol pulse of
Oxygen in Argon
yielding 1428 mJ
corresponding to
3173 KJ/mol (= 5.3
times the heat of
formation of water

FIGURE 1

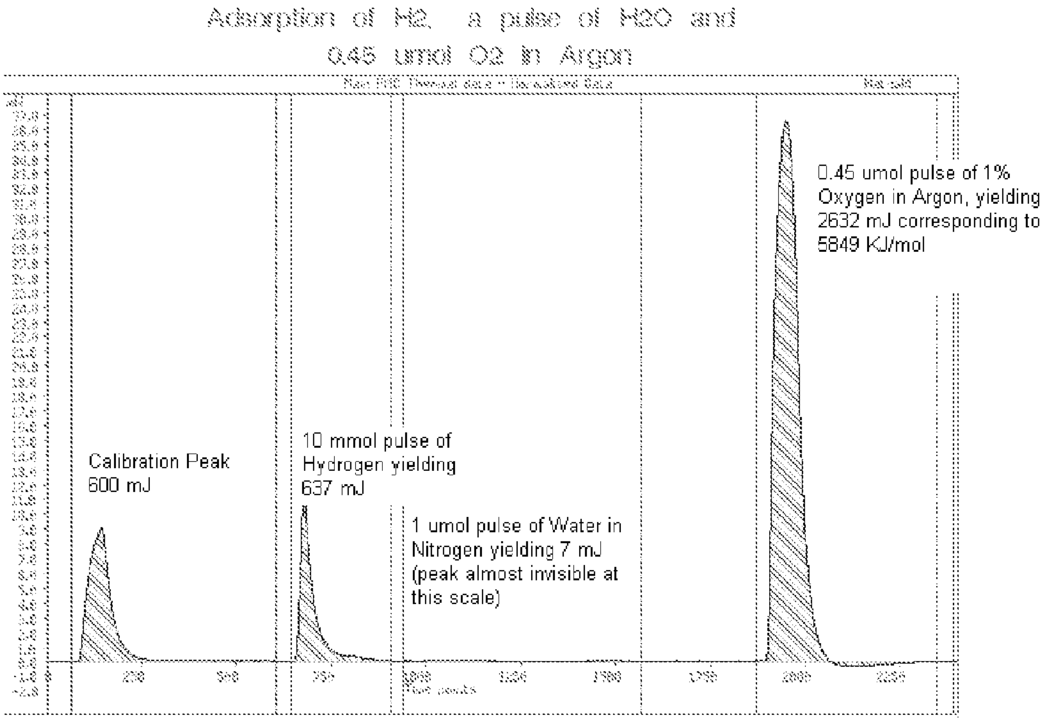
Adsorption of H2, a pulse of H2O and
0.45 umol O2 in Argon
Calibration Peak
600 mJ
10 mmol pulse of
Hydrogen yielding
637 mJ
1 umol pulse of Water in
Nitrogen yielding 7 mJ
(peak almost invisible at
this scale)
0.45 umol pulse of 1%
Oxygen in Argon, yielding
2632 mJ corresponding to
5849 KJ/mol
250
500
750
1000
1250
1500
1750
2000
2250

FIGURE 2

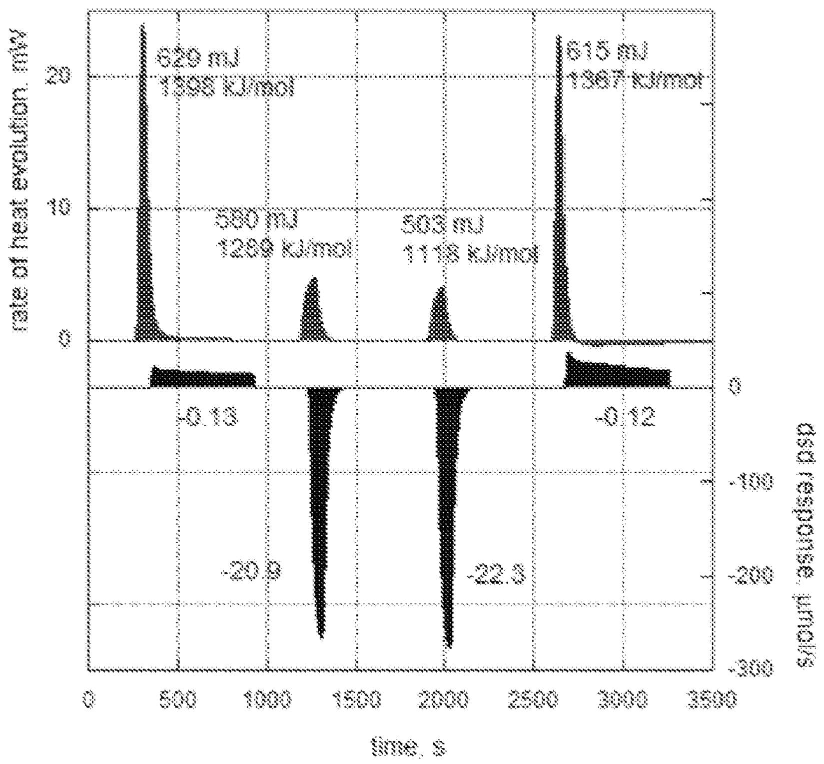
rate of heat evolution, mW
20
10
0
629 mJ
1398 kJ/mol
580 mJ
1289 kJ/mol
503 mJ
1118 kJ/mol
615 mJ
1367 kJ/mol
-0.13
-20.9
-22.5
-0.12
0
-100
-200
-300
dsp response, µmol/s
0
500
1000
1500
2000
2500
3000
3500
time, s

FIGURE 3

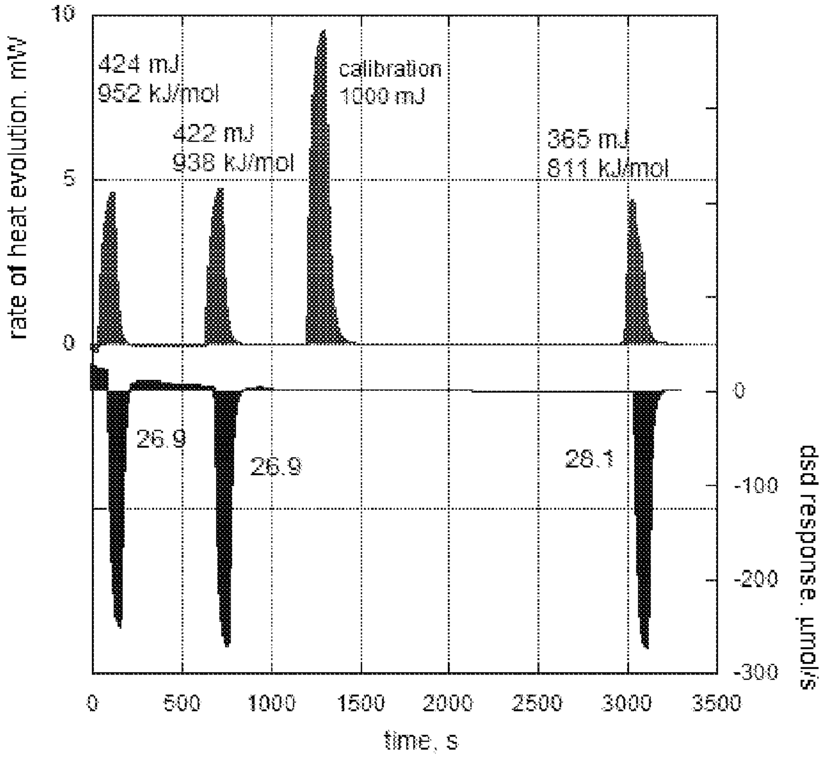

FIGURE 4

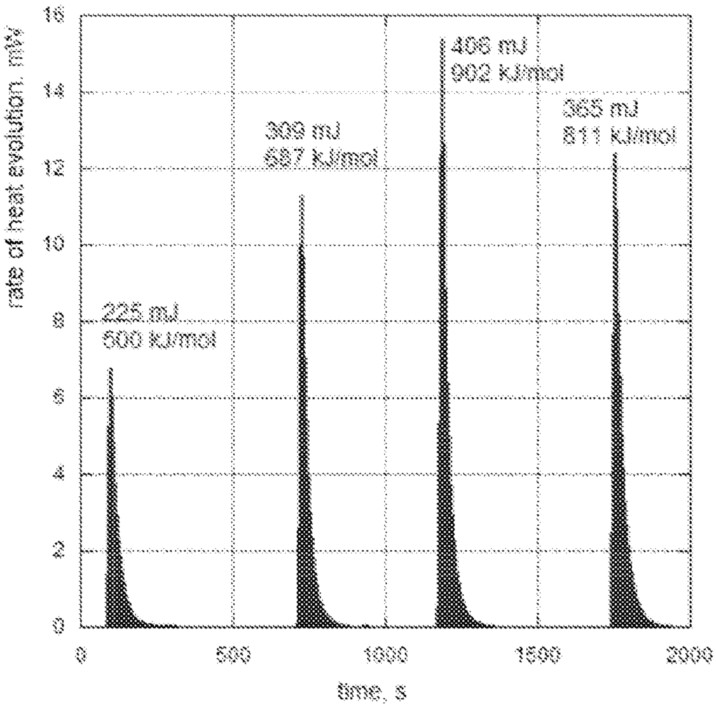

FIGURE 5

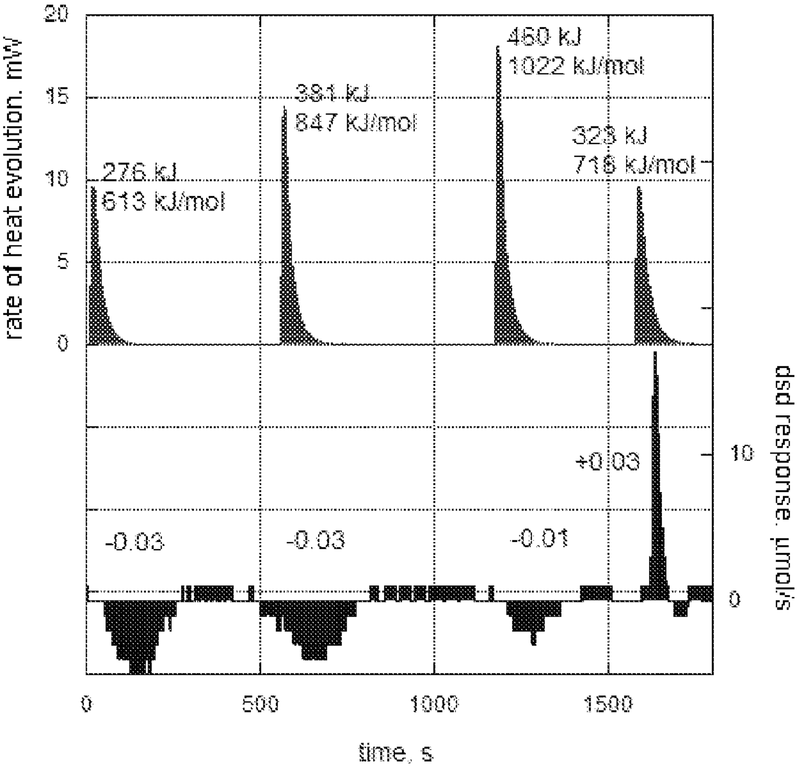
20
15
10
5
0
rate of heat evolution, mW
276 kJ
613 kJ/mol
381 kJ
847 kJ/mol
460 kJ
1022 kJ/mol
323 kJ
716 kJ/mol
-0.03
-0.03
-0.01
+0.03
10
0
dsd response, µmol/s
0
500
1000
1500
time, s

FIGURE 6