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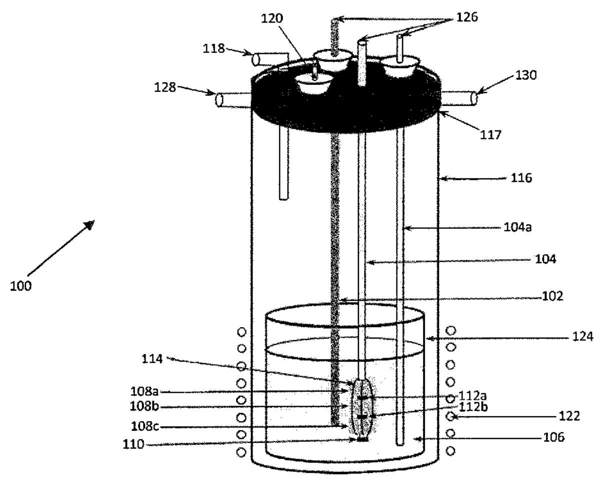
(54) Title: AN ELECTROCHEMICAL METHOD OF REDUCING METAL OXIDE

Figure 1



(57) Abstract: There is provided a method of electrochemically reducing multiple metal oxide pellets simultaneously, the method comprising: contacting an anode and a cathode with multiple metal oxide pellets with an electrolyte, wherein the multiple metal oxide pellets are secured to the cathode; and applying an electrical potential between the anode and the cathode to reduce multiple metal oxides comprised in the multiple metal oxide pellets to its respective metals. There is also provided an electrochemical cell for electrochemically reducing multiple metal oxide pellets simultaneously.

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An electrochemical method of reducing metal oxide

Technical Field

The present invention relates to a method of electrochemically reducing multiple metal oxide pellets simultaneously. The present invention also provides an electrochemical cell for electrochemically reducing multiple metal oxide pellets simultaneously.

Background

Electrochemical reduction of metals is commonly known in the art. In particular, electrolytic processes may be used, for example, to reduce metal compounds or semi-metal compounds to metals, semi-metals, or partially-reduced compounds, or to reduce mixtures of metal compounds to form alloys.

There has been great interest in the direct production of metal by direct reduction of a solid metal oxide feedstock. However, the problem with the prior art methods is that the methods are a low-throughput synthesis of metals since only one metal oxide can be processed at a time.

Thus, there is a need for an improved method of producing metal.

Summary of the invention

The present invention seeks to address these problems, and/or to provide a method for simultaneously electrochemically reducing multiple metal oxide pellets to enable efficient production of metals at high throughput. The present invention also provides an electrochemical cell suitable for simultaneously electrochemically reducing multiple metal oxide pellets.

According to a first aspect, the present invention provides a method of electrochemically reducing multiple metal oxide pellets simultaneously, the method comprising:

- contacting an anode and a cathode with multiple metal oxide pellets with an electrolyte, wherein the multiple metal oxide pellets are secured to the cathode; and
- applying an electrical potential between the anode and the cathode to reduce multiple metal oxides comprised in the multiple metal oxide pellets to its respective metals.

According to a particular aspect, each of the multiple metal oxide pellets may have the same or different composition from each other.

Each of the multiple metal oxide pellets may comprise at least one metal oxide. The at least one metal oxide may be an oxide of any suitable metal. For example, the at least one metal oxide may be, but not limited to: titanium oxide (TiO_2), cobalt oxide (CoO), chromium oxide (Cr_2O_3), iron oxide (Fe_2O_3), nickel oxide (NiO), aluminium oxide (Al_2O_3), manganese oxide (MnO_2), niobium pentoxide (Nb_2O_5), tin (IV) oxide (SnO_2), tantalum pentoxide (Ta_2O_5), terbium (III) oxide (Tb_2O_3), lanthanum oxide (La_2O_3), zirconium dioxide (ZrO_2), silicon dioxide (SiO_2), vanadium pentoxide (V_2O_5), vanadium dioxide (VO_2), vanadium trioxide (V_2O_3), ytterbium oxide (Yb_2O_3), dysprosium oxide (Dy_2O_3), erbium oxide (Er_2O_3), samarium oxide (Sm_2O_3), gadolinium oxide (Gd_2O_3), germanium dioxide (GeO_2), magnesium oxide (MgO), neodymium oxide (Nd_2O_3), lithium superoxide (LiO_2), cerium oxide (CeO_2), copper oxide (CuO), uranium dioxide (UO_2), triuranium octoxide (U_3O_8), hafnium dioxide (HfO_2), tungsten trioxide (WO_3), $NiAl_2O_4$, $SrTiO_3$, $FeTiO_3$, $CaWO_4$, or a combination thereof.

According to a particular aspect, each of the multiple metal oxide pellets may be porous. For example, each of the multiple metal oxide pellets may have a porosity of 5-60%.

Each of the multiple metal oxide pellets may be of any suitable size and shape. For example, the pellet may have an average size of 2-100 mm.

The cathode may be any suitable cathode. For example, the cathode may comprise, but is not limited to, titanium (Ti), stainless steel, molybdenum, nickel, iron-chromium-aluminium (FeCrAl) alloy, or a combination thereof.

The anode may be any suitable anode. For example, the anode may comprise, but is not limited to, graphite, glassy carbon, $CaRuO_3$, SnO_2, or a combination thereof.

The electrolyte may be any suitable electrolyte for the purposes of the present invention. According to a particular aspect, the electrolyte may comprise a molten salt. The molten salt may be any suitable molten salt. For example, the molten salt may be, but not limited to, calcium chloride ($CaCl_2$), lithium chloride (LiCl), lithium oxide (Li_2O), sodium chloride (NaCl), calcium oxide (CaO), lithium bromide (LiBr), potassium bromide (KBr), cesium bromide (CsBr), calcium bromide ($CaBr_2$), potassium chloride (KCl), potassium bromide (KBr), or a combination thereof.

According to a particular aspect, the electrolyte may be in a molten state. Accordingly, the method may further comprise heating the electrolyte prior to the contacting. In particular, the heating may comprise melting the electrolyte to a molten state. The electrolyte may be at any suitable temperature. For example, the electrolyte may be at a temperature of 400-1200°C prior to the contacting.

The method may be carried out under an inert atmosphere. For example, the inert atmosphere may comprise, but is not limited to, argon.

The applying may be for a suitable period of time. According to a particular aspect, the applying may be for a pre-determined period of time.

The method may further comprise collecting the multiple metal oxide pellets following the applying to recover the metals.

According to a second aspect, the present invention provides an electrochemical cell for electrochemically reducing multiple metal oxide pellets simultaneously, the cell comprising:

- an anode;
- a cathode comprising multiple metal oxide pellets secured to the cathode;
- an electrolyte; and
- a power supply for applying an electrical potential between the anode and the cathode to reduce multiple metal oxides comprised in the multiple metal oxide pellets to its respective metals.

The anode, cathode and electrolyte may be any suitable anode, cathode and electrolyte, respectively. In particular, the anode, cathode and electrolyte may be as described above in relation to the first aspect.

Each of the multiple metal oxide pellets may be any suitable metal oxide pellet. In particular, each of the multiple metal oxide pellets may be as described above in relation to the first aspect.

Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments, the description being with reference to the accompanying illustrative drawings. In the drawings:

Figure 1 shows a schematic representation of an electrochemical cell according to one embodiment of the present invention;

Figure 2 shows the XRD analysis of a reduced metal obtained after electrochemical reduction of a metal oxide pellet according to one embodiment of the present invention;

Figure 3 shows the XRD analysis of a reduced metal ally obtained after electrochemical reduction of a metal oxide pellet according to one embodiment of the present invention; and

Figure 4 shows the XRD analysis of a reduced metal alloy obtained after electrochemical reduction of a metal oxide pellet according to one embodiment of the present invention.

Detailed Description

As explained above, there is a need for an improved method of producing metal.

In general terms, the present invention provides an efficient production of metals at high-throughput. This provides several advantages such as reducing lead time for material discovery, as well as providing a more practical way of scaling up production of metals. The method of the present invention may also be suitable for producing metal alloys by reducing multiple elemental compositions. The present invention also provides an electrochemical cell to efficiently produce the metals.

According to a first aspect, the present invention provides a method of electrochemically reducing multiple metal oxide pellets simultaneously, the method comprising:

- contacting an anode and a cathode with multiple metal oxide pellets with an electrolyte, wherein the multiple metal oxide pellets are secured to the cathode; and

- applying an electrical potential between the anode and the cathode to reduce multiple metal oxides comprised in the multiple metal oxide pellets to its respective metals.

For the purposes of the present invention, the term metal may be defined to encompass all such products, such as metals, semi-metals, alloys, intermetallics. Metal may also be considered, where appropriate, to include partially reduced products.

According to a particular aspect, each of the multiple metal oxide pellets may have the same or different composition from each other. According to a particular embodiment, each of the multiple metal oxide pellets may be the same as each other. According to another particular embodiment, each of the multiple metal oxide pellets may be different from each other. According to yet another embodiment, some of metal oxide pellets may be the same while other within the multiple metal oxide pellets may be different.

Each of the multiple metal oxide pellets may comprise at least one metal oxide. The at least one metal oxide may be an oxide of any suitable metal. For example, the at least one metal oxide may be, but not limited to: titanium oxide (TiO_2), cobalt oxide (CoO), chromium oxide (Cr_2O_3), iron oxide (Fe_2O_3), nickel oxide (NiO), aluminium oxide (Al_2O_3), manganese oxide (MnO_2), niobium pentoxide (Nb_2O_5), tin (IV) oxide (SnO_2), tantalum pentoxide (Ta_2O_5), terbium (III) oxide (Tb_2O_3), lanthanum oxide (La_2O_3), zirconium dioxide (ZrO_2), silicon dioxide (SiO_2), vanadium pentoxide (V_2O_5), vanadium dioxide (VO_2), vanadium trioxide (V_2O_3), ytterbium oxide (Yb_2O_3), dysprosium oxide (Dy_2O_3), erbium oxide (Er_2O_3), samarium oxide (Sm_2O_3), gadolinium oxide (Gd_2O_3), germanium dioxide (GeO_2), magnesium oxide (MgO), neodymium oxide (Nd_2O_3), lithium superoxide (LiO_2), cerium oxide (CeO_2), copper oxide (CuO), uranium dioxide (UO_2), triuranium octoxide (U_3O_8), hafnium dioxide (HfO_2), tungsten trioxide (WO_3), $NiAl_2O_4$, $SrTiO_3$, $FeTiO_3$, $CaWO_4$, or a combination thereof.

According to a particular aspect, the multiple metal oxide pellets may comprise at least one pellet comprising TiO_2, at least one pellet comprising CoO, Cr_2O_3, Fe_2O_3 and NiO, and/or at least one pellet comprising Al_2O_3, CoO, Cr_2O_3, Fe_2O_3 and NiO.

The method of the present invention may be suitable for forming any metal or its alloy. For example, the method may be for reducing metal oxides comprised in the multiple metal oxide pellets to form titanium (Ti), cobalt (Co), chromium (Cr), iron (Fe), nickel (Ni), aluminium (Al), or an alloy thereof. In particular, the method may be for forming at least one of Ti, CoCrFeNi or $Al_xCoCrFeNi$, wherein x is 0.1 to 2.0.

For example, when it is desired to form pure Ti, the multiple metal oxide pellets may comprise TiO_2. When it is desired to form high entropy alloy CoCrFeNi, the multiple metal oxide pellets may comprise CoO, Cr_2O_3, Fe_2O_3 and NiO. When it is desired to form high entropy alloy $Al_xCoCrFeNi$, the multiple metal oxide pellets may comprise Al_2O_3, CoO, Cr_2O_3, Fe_2O_3 and NiO.

According to a particular aspect, each of the multiple metal oxide pellets may be porous. If the pellets are too porous, they may not be mechanically strong enough to withstand handling and would crumble into the electrolyte during the electrochemical reduction of the pellet. On the other hand, if the pellets are not porous enough, the electrochemical reduction process would be very slow. Accordingly, each of the multiple metal oxide pellets may have a suitable porosity. For example, each of the multiple metal oxide pellets may have a porosity of 5-60%. In particular, the porosity may be 10-56%, 15-55%, 20-50%, 25-48%, 30-45%, 35-40%. Even more in particular, the porosity may be 45-60%.

Each of the multiple metal oxide pellets may be of any suitable size and shape. For the purposes of the present invention, a pellet may be defined as a compressed metal oxide having any suitable size and shape, wherein the pellet may comprise at least one metal oxide.

Examples of suitable shapes of the pellets may include, but is not limited to, annular, spherical, elliptical, cubic, pyramidal, cylindrical. In particular, the pellet may be annular.

The pellet may have an average size of 2-100 mm. For the purposes of the present invention, average size may refer to at least one of the height, width, or diameter of the pellet. In particular, the pellet may have an average size of 5-90 mm, 10-85 mm, 15-80 mm, 20-75 mm, 25-70 mm, 30-65 mm, 35-60 mm, 40-55 mm, 45-50 mm. Even more in particular, the pellet may have an average size of 10-20 mm.

According to a particular embodiment, the pellet may be annular having an outer diameter of about 15 mm, an inner diameter of about 5 mm and a thickness of about 3-3.5 mm.

The multiple metal oxide pellets may be prepared by any suitable method. For example, the preparing of the metal oxide pellets may comprise sintering each of the multiple metal oxide pellets. The sintering may be by any suitable method. The advantage of this is that the pellets are able to maintain structural integrity so that the pellet does not fall apart before or during the electrochemical reduction of the pellet.

Each of the multiple metal oxide pellets may be secured to the cathode by any suitable manner. The pellets may be secured to the cathode to ensure that the metal oxide pellets are in constant electrical contact with the cathode at all times during the method.

According to a particular aspect, the cathode may be screw-threaded so that each of the multiple metal oxide pellets may be secured to the cathode by a nut at the cathode. In this way, the pellets are prevented from dropping into the electrolyte and this also enables the surface area of the pellets in contact with the cathode to increase. Further, each of the multiple metal oxide pellets may be separated from one another by any suitable means. For example, the pellets may be separated by using a small segment of wire, such as, but not limited to, iron-chromium-aluminium (FeCrAl) alloy wire.

The multiple metal oxide pellets may be further secured by a wire cage so that the pellets are prevented from falling off the cathode in case the pellets crack during the method. The wire cage may be of any suitable material. For example, the wire cage may be of FeCrAl alloy wire.

The cathode may be any suitable cathode. For example, the cathode may comprise, but is not limited to, titanium (Ti), stainless steel, molybdenum, nickel, iron-chromium-aluminium (FeCrAl) alloy, or a combination thereof.

The anode may be any suitable anode. For example, the anode may comprise, but is not limited to, graphite, glassy carbon, $CaRuO_3$, SnO_2, or a combination thereof. In particular, when carbon based anodes are used, carbon dioxide may be evolved at the anode during the electrochemical reduction. When inert anodes, such as $CaRuO_3$,

SnO_2 are used, oxygen may be evolved at the anode during the electrochemical reduction.

The electrolyte may be any suitable electrolyte for the purposes of the present invention. According to a particular aspect, the electrolyte may comprise a molten salt. The molten salt may be any suitable molten salt to facilitate reduction of the multiple metal oxide pellets. For example, the molten salt may comprise an alkali halide salt, an alkaline earth metal halide salt, an alkali oxide, or combinations thereof. In particular, the molten salt may comprise, but is not limited to, lithium chloride (LiCl), lithium oxide (Li_2O), sodium chloride (NaCl), calcium chloride ($CaCl_2$), calcium oxide (CaO), lithium bromide (LiBr), potassium bromide (KBr), cesium bromide (CsBr), calcium bromide ($CaBr_2$), potassium chloride (KCl), potassium bromide (KBr), or a combination thereof. Even more in particular, the molten salt may be $CaCl_2$ or a combination of $CaCl_2$ and CaO.

According to a particular aspect, the electrolyte may comprise a molten salt and an additive. The additive may be any suitable additive. For example, the additive may be an alkali earth metal oxide. In particular, the additive may be CaO.

The additive may be added in any suitable amount. For example, the additive may be added at a weight concentration of 0.25-5.0 weight% of the electrolyte. In particular, the additive may be added at a weight concentration of 0.5-4.5 wt %, 1.0-4.0 wt %, 1.5-3.5 wt %, 2.0-3.0 wt %, 2.5-2.8 wt % of the electrolyte. Even more in particular, the additive may be added at a weight concentration of 0.1-1.0 wt % of the electrolyte.

According to a particular embodiment, the electrolyte may comprise $CaCl_2$ and CaO. The CaO may constitute 0.25-5.0 weight % of the electrolyte. In particular, the CaO may constitute 0.5-4.5 wt %, 1.0-4.0 wt %, 1.5-3.5 wt %, 2.0-3.0 wt %, 2.5-2.8 wt % of the electrolyte. The $CaCl_2$ may constitute the remainder of the electrolyte. Even more in particular, the electrolyte may comprise 2.0 wt % CaO.

According to a particular aspect, the electrolyte may be in a molten state during the method. Accordingly, the method may further comprise heating the electrolyte prior to the contacting. The heating may be by any suitable means. In particular, the heating may comprise melting the electrolyte to a molten state. The electrolyte may remain in the molten state during the method. Therefore, the temperature of the electrolyte may be maintained at or above a melting temperature of the molten salt comprised in the electrolyte. The electrolyte may be at any suitable temperature. For example, the electrolyte may be at a temperature of 400-1200°C prior to the contacting. In particular, the temperature may be 420-1150°C, 450-1100°C, 500-1000°C, 550-950°C, 600-900°C, 650-850°C, 700-800°C. Even more in particular, the temperature may be about 900°C.

The method may be carried out under an inert atmosphere. For example, the inert atmosphere may comprise an inert gas such as, but not limited to, argon, helium, or a combination thereof. In particular, the inert atmosphere may comprise argon.

The applying an electrical potential between the anode and the cathode may be by any suitable means. For example, the electrical potential may be applied by, but not limited to, a DC power supply.

The applying may be for a suitable period of time. According to a particular aspect, the applying may be for a pre-determined period of time. For example, the pre-determined period of time may be 6-48 hours. In particular, the pre-determined period of time may be 12-45 hours, 18-42 hours, 24-36 hours, 30-32 hours. Even more in particular, the pre-determined period of time may be about 24 hours.

The applying results in a provision of a polarization field and a driving force for moving oxide ions dissolved from the metal oxide pellet at the cathode to the anode, facilitating reduction of the metal oxide at the cathode.

In particular, the electrolyte may facilitate reduction of the metal oxide pellets. For example, the metal oxide pellets may be reduced at the cathode, according to Equation (1) below:

$$M_yO_x + ze^- \rightarrow yM + z/xO_2 \qquad (1),$$

wherein M is a metal, M_yO_x is the metal oxide, x is the stoichiometric amount of oxygen for the particular metal oxide, y is the stoichiometric amount of the metal in the metal oxide, and z is the stoichiometric amount of electrons for balancing the chemical reaction. The electrons are provided by applying an electrical potential between the anode and the cathode. The composition of the metal formed at the cathode may vary based on the composition of the metal oxide pellets.

The oxide ions generated at the cathode may be transported from the cathode to the anode responsive to exposure to the applied electrical field. The oxide ions may be oxidized at the anode according to Equation (2) below:

$$2O^{2-} \rightarrow O_2\,(g) + 4e^- \qquad (2).$$

The oxygen gas generated at the anode may be evolved at the anode. The electrons may be returned to the anode surface.

The method may further comprise collecting the pellets following the applying to recover the metals. The recovering of the metals from the pellets may be by any suitable method. For example, the pellets may be cleaned using suitable solvents and dried to obtain the metal. The solvents may be, but not limited to, hydrochloric acid (HCl), distilled water, or a combination thereof. The pellets may be dried by any suitable means. For example, the pellets may be dried in an oven at a suitable temperature such as, but not limited to, 100°C.

According to a particular aspect, the method may comprise a pre-electrolysis prior to the electrochemical reduction of the metal oxide pellets. The pre-electrolysis comprises applying an electrical potential between the anode and a pre-electrolysis cathode. The pre-electrolysis cathode may be any suitable cathode which does not comprise any metal oxide pellets. The pre-electrolysis may eliminate any trace amounts of impurities which may be present in the electrolyte. The pre-electrolysis may be carried out for a suitable period of time.

According to a second aspect, the present invention provides an electrochemical cell for electrochemically reducing multiple metal oxide pellets simultaneously, the cell comprising:

- an anode;
- a cathode comprising multiple metal oxide pellets secured to the cathode;
- an electrolyte; and
- a power supply for applying an electrical potential between the anode and the cathode to reduce multiple metal oxides comprised in the multiple metal oxide pellets to its respective metals.

The anode, cathode and electrolyte may be any suitable anode, cathode and electrolyte, respectively. In particular, the anode, cathode and electrolyte may be as described above in relation to the first aspect.

Each of the multiple metal oxide pellets may be any suitable metal oxide pellet. In particular, each of the multiple metal oxide pellets may be as described above in relation to the first aspect.

A schematic representation of the cell according to an embodiment of the present invention is shown in Figure 1.

Figure 1 provides a simplified schematic of an electrochemical cell 100 for electrochemically reducing multiple metal oxide pellets simultaneously. The electrochemical cell 100 may comprise an anode 102, a cathode 104, a molten salt electrolyte 106. The anode 102 and the cathode 104 may be in contact with the molten salt electrolyte 106. The cathode 104 may comprise multiple metal oxide pellets (shown as 108a, 108b and 108c). Each of the metal oxide pellets 108a, 108b and 108c may be of the same or different composition. The metal oxide pellets 108a, 108b and 108c may be secured to the cathode 104 by any suitable means, such as a metal nut 110. In this particular embodiment, the cathode 104 may be threaded in order to secure the metal oxide pellets 108a, 108b and 108c. However, any other suitable means of securing the metal oxide pellets to the cathode may be used.

Each of the metal oxide pellets 108a, 108b and 108c may be separated from each other as shown in Figure 1. For example, the metal oxide pellets 108a, 108b and 108c may each be separated from each other by placing wire 112a between the metal oxide pellets 108a and 108bm and by placing wire 112b between metal oxide pellets 108b and 108c. The metal oxide pellets 108a, 108b and 108c may be further secured to the cathode 104 by wire 114 which forms a cage-like structure to prevent the metal oxide pellets 108a, 108b and 108c from detaching from the cathode 104. In this way, the metal oxide pellets 108a, 108b and 108c are in constant electrical contact with the cathode 104. The wire 112a, 112b and 114 may be any suitable wire. For example, the wire 112a, 112b and 114 may be as described above. In particular, the wire 112a, 112b and 114 may be iron-chromium-aluminium (FeCrAl) alloy wire.

The electrochemical cell 100 may optionally be contained within a gas-tight enclosure 116, which may include a gas inlet 118 and a gas outlet 120. The gas-tight enclosure

116 may be made gas-tight by providing an O-ring 117 for sealing the enclosure 116. However, any other suitable sealing means may be used for sealing the enclosure 116.

The gas inlet 118 may be configured for providing, for example, a gas to the enclosure 116 for maintaining a gas pressure within the enclosure 116. Gases may be removed from the enclosure 116 via the gas outlet 120. The gas may comprise an inert gas, such as that described above.

The enclosure 116 may further include heating means 122 for heating or maintaining a temperature of the molten salt electrolyte 106 in the electrochemical cell 102. The heating means 122 may be any suitable heating means such as, but not limited to, a heater, a heating element, or a combination thereof.

The molten salt electrolyte 106 may be comprised in a crucible 124. The crucible 124 may be any suitable crucible. For example, the crucible 124 may be formed of a metal, glassy carbon, ceramic, a metal alloy, or any other suitable material. The crucible 124 may also be formed of a non-metallic material, such as alumina (Al_2O_3), magnesia (MgO), glassy carbon, graphite, boron nitride, or combinations thereof. In particular, the crucible 124 may be formed from any suitable insulating refractory material. Even more in particular, the crucible 124 may be formed of alumina.

As noted above, molten salt electrolyte 106 may be disposed in the crucible 124, in which the anode 102 and the cathode 104 are also located. In some embodiments, the electrochemical cell 100 may further comprise a pre-electrolysis cathode 104a located in crucible 124 and configured for removing impurities in the electrolyte 106. The pre-electrolysis cathode 104a does not comprise any metal oxide pellets. The pre-electrolysis cathode 104a may be lifted out of the electrolyte 106 prior to the electrochemical reduction of metal oxide pellets. In particular, the system of Figure 1 is such that the pre-electrolysis cathode 104a and the cathode 104 comprising the metal oxide pellets 108a, 108b and 108c are not present in the electrolyte 106 at the same time.

The electrochemical cell 100 may further comprise connections 126 to a power supply. The power supply may be any suitable power supply such as a DC power supply. The connections 126 may be electrically coupled to each of the anode 102, the cathode 104, and the pre-electrolysis cathode 104a. The connections 126 may be configured to provide an electric potential between the anode 102 and the cathode 104, and between the anode 102 and the pre-electrolysis cathode 104a. The difference between the electric potential of the anode 102 and the electric potential of the cathode 104 may be referred to as a cell potential of the electrochemical cell 100.

The electric potential applied between the anode 102 and the cathode 104 may deposit at least one metal by reduction of the metal oxide pellets 108a, 108b and 108c simultaneously since all the metal oxide pellets 108a, 108b and 108c are provided on the cathode 104.

The electrochemical cell 100 may further comprise a cooling inlet 128 and a cooling outlet 130. The cooling inlet 128 and the cooling outlet 130 may be used for passing cooling liquid around the electrochemical cell 102 to cool down the electrochemical cell 102 following electrochemical reduction of the metal oxide pellets 108a, 108b and 108c and/or for maintaining the temperature of the molten salt electrolyte 106 during the electrochemical reduction method. The cooling liquid may be any suitable liquid. For example, the cooling liquid may be water.

Having now generally described the invention, the same will be more readily understood through reference to the following embodiment which is provided by way of illustration, and is not intended to be limiting.

Example

Example 1 – Electrochemical reduction of TiO_2 pellets in $CaCl_2$ electrolyte comprising CaO

Preparation of TiO_2 pellets

5% poly(vinyl butyral) (molecular weight 30000-35000, Arcos Organics) was dissolved in isopropanol and added to TiO_2 powder (40982-08, Kanto Chemical Co Inc.). The mixture was ground in a mortar until dry and sieved. 1 g of the resultant mixture was uniaxially pressed at 25-100 MPa in a hollow die and sintered at 900°C in air for 2 hours. The resultant pellet had an outer diameter of 15 mm and 5 mm inner diameter with a thickness of about 3-3.5 mm. The porosity of the pellets varied between 48-56%.

The pellets were then secured to a cathode to ensure that the pellets were in constant electrical contact with the cathode. The cathode was screw-threaded and the pellets were secured onto the cathode by a metal nut at the end of the cathode. In this way, the pellets were prevented from dropping into the electrolyte when the cathode is placed in an electrolyte. This also resulted in an increase in the surface area of the pellets in contact with the cathode due to the enhanced contact with the metal nut. Each pellet was separated from the next pellet by a small segment of iron-chromium-aluminium (FeCrAl) alloy wire (Kanthal wire) or metal nut. The pellets were further secured by a cage of iron-chromium-aluminium (FeCrAl) alloy wire to prevent the pellets from falling off the cathode in case the pellets cracked during the electrochemical reduction method.

Preparation of $CaCl_2$ electrolyte with 2 mol% CaO

213 g of anhydrous calcium chloride (746495, Sigma-Aldrich) and 2.3 g (2 mol%) of CaO (208159 Sigma-Aldrich) was mixed and added into an alumina crucible. The alumina crucible was placed in a vacuum oven and dried at 120°C under vacuum overnight.

Electrochemical reduction

The electrochemical reduction was performed in an electrochemical cell as shown in Figure 1. An alumina crucible comprising the electrolyte was first slowly lowered into an Inconel reactor and the reactor was closed with a stainless steel cover. Argon was purged into the reactor continuously to maintain an inert atmosphere. A graphite anode, the Ti cathode comprising the metal oxide pellets, and a pre-electrolysis Ti cathode were fixed to the reactor but not lowered into the crucible. The electrolyte was then melted at 900°C and pre-electrolysis was performed by lowering the pre-electrolysis Ti cathode and the graphite anode into the molten electrolyte for pre-electrolysis. The electrodes were connected to a DC power supply and 1.5 V was applied for several hours until a small and time-independent current was achieved. Pre-electrolysis was performed to eliminate the trace amounts of impurities such as water and calcium hydroxide from the electrolyte.

Following that, the pre-electrolysis cathode was lifted up and the Ti cathode with the metal oxide pellets was lowered into the electrolyte. The electrolysis was performed at 3.2 V for about 24 hours. After the reaction had completed, the electrodes were lifted up and the setup was allowed to cool to room temperature.

The pellets were detached from the cathode and thoroughly rinsed with tap water and then cleaned with dilute hydrochloric acid and distilled water. The pellets were then dried in a vacuum oven at 100°C.

Figure 2 shows the XRD analysis for the final product obtained. As shown in Figure 2, TiO_2 pellets were successfully reduced to Ti metal as the XRD pattern matched that of pure titanium (*Electrochimica Acta*, 2005, 51:66-76). Approximately 0.6 g of Ti was obtained per pellet.

<u>Example 2 – Electrochemical reduction of mixed oxide pellets containing CoO, Cr_2O_3, Fe_2O_3 and NiO in $CaCl_2$ electrolyte</u>

Preparation of mixed oxide pellets containing CoO, Cr_2O_3, Fe_2O_3 and NiO

Cobalt oxide, chromium oxide, iron oxide and nickel oxide were ball milled with a ball-power-ratio of 18 at 200 rpm for 5 hours (molar ratio 1:1:1:1). Pre-determined molar 1% by mass of PVA and 0.5% by mass of PEG (M.W. 14000) was then dissolved in isopropanol and added to the mixture. The mixture was ground in a mortar until dry. 1 g of the resultant mixture was uniaxially pressed at 25-100 MPa in a hollow die and sintered at 900°C in air for 2 hours. The resultant pellet had an outer diameter of about 15 mm an inner diameter of about 5 mm with a thickness of about 3-3.5 mm.

Loading the pellet onto the electrochemical reactor

The cathode was screw-threaded and the pellets were secured onto the cathode by a metal nut at the end of the cathode to prevent the pellets from dropping into the electrolyte and to also increase the surface area in contact with the cathode due to the enhanced contact with the metal nut. Each pellet was then separated from the next pellet by a metal nut. The pellets were secured again by a cage of Kanthal wire to prevent the pellets from falling off the cathode in case the pellets cracked.

Preparation of $CaCl_2$ electrolyte

180 g of anhydrous calcium chloride (746495, Sigma-Aldrich) was added to an alumina crucible and placed in a vacuum oven and dried at 200°C under vacuum overnight.

Electrochemical reduction

The electrochemical reduction was carried out similarly to that as described in Example 1, except that pre-electrolysis was carried out at a DC power supply of 2.8 V. Thereafter, electrolysis was performed at 3.0 V over 24 hours.

After the reaction had completed, the electrodes were lifted up and the setup was allowed to cool to room temperature. The pellets were thoroughly rinsed with DI water and acetone, and then dried in a vacuum oven at 60°C.

XRD analysis of the final product showed that the metal oxide pellets were successfully reduced. Figure 3 shows the XRD analysis of the final product after the electrochemical reduction which tallies with the XRD of a face-centred cubic CoCrFeNi structure (*Journal of Alloys and Compounds,* 776, **2019**, 133-141). Thus, mixed oxide pellets were successfully reduced to the high entropy alloy CoCrFeNi. The oxygen content of the alloy was approximately 0.5-0.8 wt %, as analysed by inert gas fusion. Approximately 0.5 g of the metal alloy was obtained per pellet.

Example 3 – Electrochemical reduction of mixed oxide pellets containing Al_2O_3, CoO, Cr_2O_3, Fe_2O_3 and NiO in $CaCl_2$ electrolyte

Preparation of mixed oxide pellets containing Al_2O_3, CoO, Cr_2O_3, Fe_2O_3 and NiO

Aluminium oxide, cobalt oxide, chromium oxide, iron oxide and nickel oxide were ball milled with a ball-power-ratio of 18 at 200 rpm for 5 hours (molar ratio x:1:1:1:1, where x = 0.1-2.0). Pre-determined molar 1% by mass of PVA and 0.5% by mass of PEG (M.W. 14000) was then dissolved in isopropanol and added to the mixture. The mixture was ground in a mortar until dry. 1 g of the resultant mixture was uniaxially pressed at 25-100 MPa in a hollow die and sintered at 900°C in air for 2 hours. The resultant pellet had an outer diameter of about 15 mm an inner diameter of about 5 mm with a thickness of about 3-3.5 mm.

Loading the pellet onto the electrochemical reactor

The pellets were secured onto the cathode in the same manner as had been done in Example 2.

Preparation of $CaCl_2$ electrolyte

The electrolyte was prepared in the same manner as in Example 2.

Electrochemical reduction

The electrochemical reduction was carried out in the same manner as described in Example 2. Thereafter, the pellets were collected and cleaned as described in Example 2.

The pellets were then crushed into powder and sintered using spark plasma sintering to consolidate the powders into a dense metal pellet. XRD analysis of the final product showed that the metal oxide pellets were successfully reduced.

Figure 4 shows the XRD analysis of the final product AlCoCrFeNi after the electrochemical reduction of the pellets. It can be seen from Figure 4 that a mixture of body centred cubic (BCC) and face-centred cubic (FCC) structures are obtained. As shown in Figure 4, the mixed oxide pellets were successfully reduced to the high entropy alloy AlCoCrFeNi.

The oxygen content of the alloy was approximately 0.1-0.2 wt %, analysed by inert gas fusion. Approximately 0.5 g of the metal alloy was obtained per pellet.

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention.

Claims

1. A method of electrochemically reducing multiple metal oxide pellets simultaneously, the method comprising:

- contacting an anode and a cathode with multiple metal oxide pellets with an electrolyte, wherein the multiple metal oxide pellets are secured to the cathode; and
- applying an electrical potential between the anode and the cathode to reduce multiple metal oxides comprised in the multiple metal oxide pellets to its respective metals.

2. The method according to claim 1, wherein each of the multiple metal oxide pellets has a porosity of 5-60%.

3. The method according to claim 1 or 2, wherein each of the multiple metal oxide pellets has same or different composition from each other.

4. The method according to any preceding claim, wherein each of the multiple metal oxide pellets comprises at least one metal oxide.

5. The method according to claim 4, wherein the at least one metal oxide is: titanium oxide (TiO_2), cobalt oxide (CoO), chromium oxide (Cr_2O_3), iron oxide (Fe_2O_3), nickel oxide (NiO), aluminium oxide (Al_2O_3), manganese oxide (MnO_2), niobium pentoxide (Nb_2O_5), tin (IV) oxide (SnO_2), tantalum pentoxide (Ta_2O_5), terbium (III) oxide (Tb_2O_3), lanthanum oxide (La_2O_3), zirconium dioxide (ZrO_2), silicon dioxide (SiO_2), vanadium pentoxide (V_2O_5), vanadium dioxide (VO_2), vanadium trioxide (V_2O_3), ytterbium oxide (Yb_2O_3), dysprosium oxide (Dy_2O_3), erbium oxide (Er_2O_3), samarium oxide (Sm_2O_3), gadolinium oxide (Gd_2O_3), germanium dioxide (GeO_2), magnesium oxide (MgO), neodymium oxide (Nd_2O_3), lithium superoxide (LiO_2), cerium oxide (CeO_2), copper oxide (CuO), uranium dioxide (UO_2), triuranium octoxide (U_3O_8), hafnium dioxide (HfO_2), tungsten trioxide (WO_3), $NiAl_2O_4$, $SrTiO_3$, $FeTiO_3$, $CaWO_4$, or a combination thereof.

6. The method according to any preceding claim, wherein the method is carried out under an inert atmosphere.

7. The method according to claim 6, wherein the inert atmosphere comprises argon.

8. The method according to any preceding claim, wherein the applying is for a pre-determined period of time.

9. The method according to any preceding claim, wherein the cathode comprises titanium (Ti), stainless steel, molybdenum, nickel, iron-chromium-aluminium (FeCrAl) alloy, or a combination thereof.

10. The method according to any preceding claim, wherein the anode comprises graphite, glassy carbon, $CaRuO_3$, SnO_2, or a combination thereof.

11. The method according to any preceding claim, wherein the pellet has an average size of 2-100 mm.

12. The method according to any preceding claim, wherein the electrolyte comprises a molten salt.

13. The method according to claim 12, wherein the molten salt comprises calcium chloride ($CaCl_2$), lithium chloride (LiCl), lithium oxide (Li_2O), sodium chloride (NaCl), calcium oxide (CaO), lithium bromide (LiBr), potassium bromide (KBr), cesium bromide (CsBr), calcium bromide ($CaBr_2$), potassium chloride (KCl), potassium bromide (KBr), or a combination thereof.

14. The method according to any preceding claim, further comprising heating the electrolyte prior to the contacting.

15. The method according to claim 14, wherein the heating comprises melting the electrolyte to a molten state.

16. The method according to any preceding claim, wherein the electrolyte is at a temperature of 400-1200°C prior to the contacting.

17. The method according to any preceding claim, further comprising collecting the multiple metal oxide pellets following the applying to recover the metals.

18. An electrochemical cell for electrochemically reducing multiple metal oxide pellets simultaneously, the cell comprising:

- an anode;
- a cathode comprising multiple metal oxide pellets secured to the cathode;
- an electrolyte; and
- a power supply for applying an electrical potential between the anode and the cathode to reduce multiple metal oxides comprised in the multiple metal oxide pellets to its respective metals.

19. The electrochemical cell according to claim 18, wherein the electrolyte is a molten electrolyte.

20. The electrochemical cell according to claim 18 or 19, wherein each of the multiple metal oxide pellets have same or different composition from each other.

21. The electrochemical cell according to any of claims 18 to 20, wherein each of the multiple metal oxide pellets comprises at least one metal oxide.

22. The electrochemical cell according to any of claims 18 to 21, wherein the at least one metal oxide is: titanium oxide (TiO_2), cobalt oxide (CoO), chromium oxide (Cr_2O_3), iron oxide (Fe_2O_3), nickel oxide (NiO), aluminium oxide (Al_2O_3), manganese oxide (MnO_2), niobium pentoxide (Nb_2O_5), tin (IV) oxide (SnO_2), tantalum pentoxide (Ta_2O_5), terbium (III) oxide (Tb_2O_3), lanthanum oxide (La_2O_3), zirconium dioxide (ZrO_2), silicon dioxide (SiO_2), vanadium pentoxide (V_2O_5), vanadium dioxide (VO_2), vanadium trioxide (V_2O_3), ytterbium oxide (Yb_2O_3), dysprosium oxide (Dy_2O_3), erbium oxide (Er_2O_3), samarium oxide (Sm_2O_3), gadolinium oxide (Gd_2O_3), germanium dioxide (GeO_2), magnesium oxide (MgO), neodymium oxide (Nd_2O_3), lithium superoxide (LiO_2), cerium oxide (CeO_2), copper oxide (CuO), uranium dioxide (UO_2), triuranium octoxide (U_3O_8), hafnium dioxide (HfO_2), tungsten trioxide (WO_3), $NiAl_2O_4$, $SrTiO_3$, $FeTiO_3$, $CaWO_4$, or a combination thereof.

Figure 1

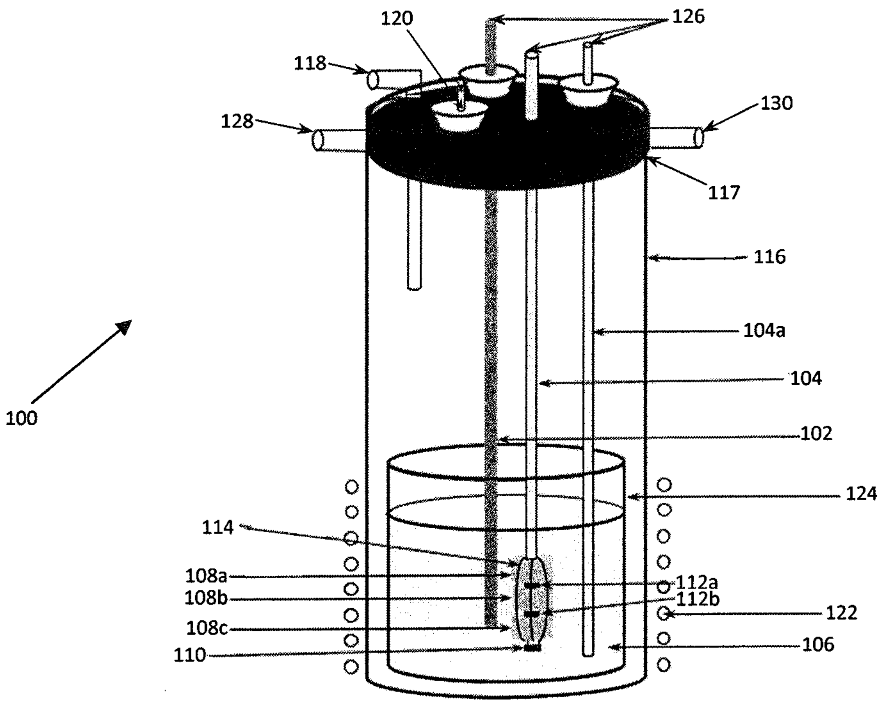

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Figure 2

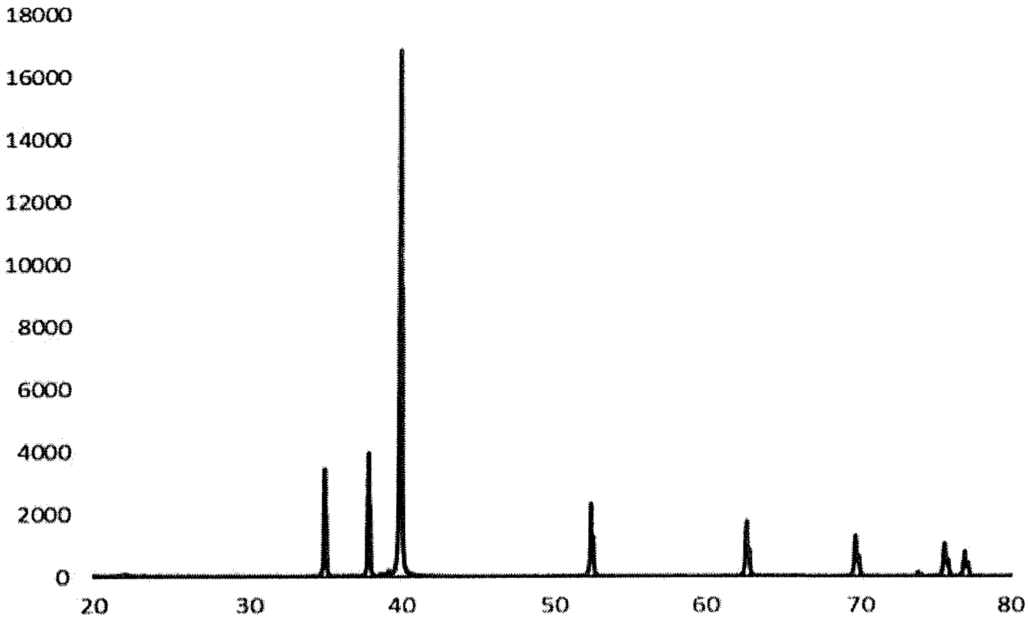


Figure 3

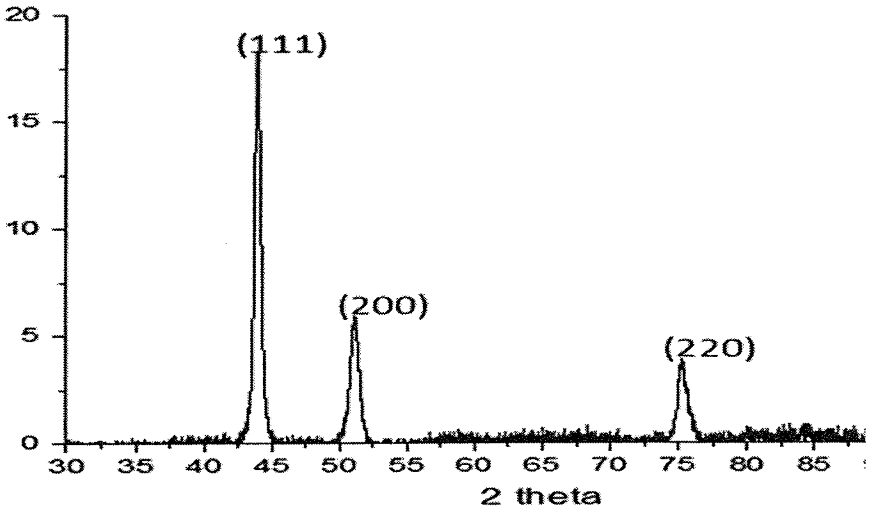
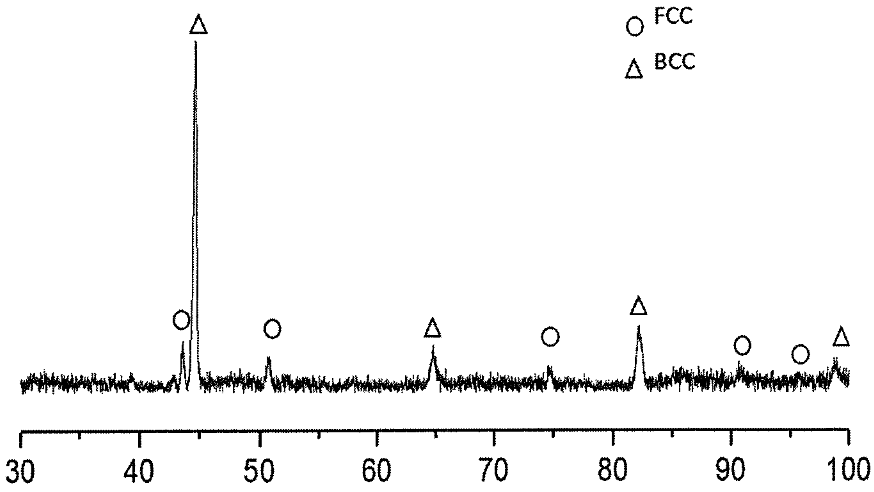


Figure 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2020/050132

A. CLASSIFICATION OF SUBJECT MATTER

C25C 3/00 (2006.01)   C25C 7/06 (2006.01)

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25C

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)

FAMPAT, CAPLUS, INSPEC, COMPENDEX using keywords: metal oxide, reduction, electrochemical, electrolytic, pellet, multi, plural, cathode, electrode and the like.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/041007 A1 (METALYSIS LIMITED) 10 April 2008 pg 14-15, Example 3; Fig. 1	1-22
X	US 2007/0295609 A1 (JEONG, S. M. ET AL.) 27 December 2007 [0012]-[0016], [0035], [0036], [0038], [0039], [0064], [0070] ; Fig. 2	1-22
X	US 2014/0165785 A1 (RASHEED, R. K. ET AL.) 19 June 2014 Examples 1, 2, [0046]-[0061], Fig. 1	1-22
X	KR 20130124846 A (KOREA ATOMIC ENERGY RES ET AL.) 15 November 2013 [0027]-[0029], [0034], Fig. 1 of the machine translation	1-22
X	US 2004/0104125 A1 (FRAY, D. J. ET AL.) 3 June 2004 [0032]-[0034], [0036], [0046], Examples; Fig. 1-2	1-22

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

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"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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04/06/2020 *(day/month/year)*	*05/06/2020* *(day/month/year)*

Name and mailing address of the ISA/SG	Authorized officer
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

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