A cyclic process for the solar photolysis of water includes a first stage in which water is reduced in the presence of a Eu^{3+} photo-oxidizable reagent producing hydrogen and spent oxidized Eu^{3+} reagent. The spent reagent (Eu^{3+}) is reduced by means of a transition metal ligand complex reductant, *RuL^{+} in a photoexcited state, such as a ruthenium pyridyl complex. Due to competing reactions between the photolysis and regeneration products, the photo-oxidation reaction must be separated from the regeneration in space and time by supporting the reagent and/or the reductant on solid supports and utilizing pH, wavelength and flow control to maximize hydrogen and oxygen production.
SOLAR PHOTOLYSIS OF WATER

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 86–568 (72 Stat. 435; 42 USC 2457).

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to solar photolysis of water to produce pure hydrogen and to various methods and apparatus for conducting such a process.

2. Description of the Prior Art

Self-sufficiency in energy is a stated national goal. Most of the proposed means to achieve this goal are either environmentally unacceptable or are not feasible, especially those not depending on fossil fuel sources. Of the available alternatives, solar energy is the most abundant, inexhaustable single resource available. However, capturing and utilizing solar energy is not simple. Methods are being sought to convert solar energy to a concentrated, storafible form of energy. A known method, photosynthesis, converts somewhat less than 1% of the sun's energy at the earth's surface to a solid fuel, i.e., plant materials, which when accumulated and transformed over geologic ages yielded fossil fuels. Current rates of use of these fossil fuels, and the particular geographic distribution and political control of major petroleum resources pose problems for nations that are net petroleum consumers. An alternate method yielding a simpler fuel, at a higher conversion, has long been desired.

Production of hydrogen by the solar photolysis of water would be an extremely desirable fuel, since it would be prepared in high purity, and the combustion product of hydrogen is water which is totally environmentally acceptable. However, it is widely believed that solar photolysis of water is not feasible, especially at quantum efficiency exceeding 1%. Douglas and Yost noted twenty four years ago in J. Chem. Phys. 4,105,517 that photolysis of water since the europium ion would be continuously exhausted by stoichiometric reaction with water, therefore the process would be unduly expensive since the amount of hydrogen generated would not economically justify the cost of the europium reagent. A cyclic photo-redox process having water and sunlight as reactants and hydrogen and oxygen and products has been disclosed in a patent application Ser. No. 658,132 filed Feb. 13, 1976, now issued on Aug. 30, 1977 as U.S. Pat. No. 4,045,315. That process utilized a soluble divalent europium photo-oxidation reagent in the hydrogen generation cycle and a complex series of steps in the dark in which a water-stable manganese oxychloride is utilized to regenerate the spent trivalent europium photo-oxidation reagent. The complexity renders the process less economic in the large scale harvesting of solar energy and the dark reaction requires use of dark panels or waiting for sunset to conduct the regeneration cycle of the process.

SUMMARY OF THE INVENTION

An improved process for the solar photolysis of water is provided in accordance with this invention. The process utilizes a photogenerated reductant capable of activation by ground level solar radiation during sunlight hours obviating the need to apply cover panels to the photoreduction reactor or to await dark periods for regeneration of the photo-oxidant reagent. The process of the invention produces improved yields of hydrogen and oxygen. The photoreductant is a single compound which reduces complexity and improves economics of the process.

The solar photolysis process of the invention utilizes transition metal ligand complexes in a photoexcited state for the reduction and regeneration of the spent photo-oxidant reagent. At least one of the photo-oxidant and the photo-reductant reagents are supported on an inert, particulate support. It is known that the complexes of transitions metals such as ruthenium with ligands such as bipyridine compounds in the photoexcited state can reduce trivalent europium and other ions. There has been no successful implementation of the reaction due to the well known competing reactions between the trivalent ruthenium ligand metal complex and the divalent europium compounds summarized as follows:

FORMATION REACTION

\[ 2H_2O + 2Eu(+) + H_2 + 20H^- + 2Eu(+) \]

REGENERATION REACTION

\[ RuL_2(+) + \text{misc.} \rightarrow RuL_2(+) + Eu (+) \]

UNDESIRABLE SIDE REACTION OF RECYCLABLE PRODUCT

\[ Eu(+) + RuL_2(+) \rightarrow [\text{misc.}] + Eu(+) + RuL_2(+) \]

UNDESIRABLE REACTION BETWEEN METAL COMPLEX AND WATER

\[ H_2O + 2RuL_2(+) \rightarrow [\text{misc.}] + O_2 + 2H^+ + 2RuL_2(+) \]

UNDESIRABLE REACTION ONCE OXYGEN IS FORMED

\[ Eu(+) + O_2 \rightarrow Eu(+) + \text{misc. products} \]

The present invention conducts the regeneration reaction in a mode which prevents the two regeneration products from interacting undesirably and also prevents undesirable side reactions between either one of the regeneration products and other materials present such as water or oxygen. A simple batch regeneration process cannot and will not produce any significant recyclable amounts of regenerated photo-oxidant. In the present invention the efficiency of the regeneration reaction is promoted by separating in time and space the regeneration reaction from the photo-oxidation reaction and by use of flow systems, pH and wavelength control to separate the products of the photoexcited reductant reaction and the photo-oxidation reaction. The invention utilizes a particulate metal oxide support for either
the photo-oxidant reagent, the photo-reductant reagent or both and may also utilize a hydrogen recombination catalyst in the photo-oxidation reaction reactor.

These and many other features and attendant advantages of the invention will become apparent as the invention becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view of a first embodiment of the invention;

FIG. 2 is a schematic view of a second embodiment of the invention; and

FIG. 3 is a schematic view of a third embodiment of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The photo-oxidant reagent is a material which absorbs strongly in the solar range at ground level and in its excited state is capable of reducing water to produce hydrogen with a quantum efficiency exceeding 0.1%. Quantum efficiency is defined as the number of moles of hydrogen produced per mole of light absorbed. Suitable water soluble transition metal cations capable of such oxidation reaction and during the reduction regeneration of the beads or the porosity of the fiber mat is governed by the acid concentration. If the pH is 4, then the maximum of spacing between surfaces may not exceed 1.0 nm. Smaller spacing may be used and will occur in a bed of beads or a glass mat, but excessively small spacing will result in a long drainage time of the solution when it is transferred to the reductant after exposure to sunlight. Hence the spacing (e.g., bead size) will be selected to meet the above specification and yet have the bed drain in a reasonable time; that time being determined by reactor size in a manner well known to chemical engineering art.

An extended photoactive range may be obtained by the use of a photochromic glass, in which the composition of the beads or fiber is altered (at the time of manufacture) to make the glass photochromic. Additions of silver halides, copper halides, iron (ferric) halides, will provide glasses with photochromic properties.

In certain embodiments of the invention the europium photo-oxidation reagent is supported on particular inert metal oxide supports having pendant oxygen functional groups capable of associating with and binding the europium ion to the support during both the photooxidation and during the reduction regeneration process. The amount of europium ion deposited on the support is determined by the quantum efficiency of the photo-oxidant.

Hydrogen production proceeds in the photo-oxidation reaction according to the following general reaction scheme:

\[ \text{M}^{z+} + \text{H}_2\text{O} \rightarrow \text{M}^{(z+1)+} + \text{H}_2 + \text{OH}^- \]

where \( z \) is the valence of the photo-oxidation reagent, \( M^{z+} \). Pure hydrogen separates from the solution as a gas. The oxidized cation \( M^{(z+1)+} \) must be regenerated by reduction.

The photogenerated reductant utilized in the present invention is a luminescent excited state of \( \text{RuL}_3 \) where \( L \) is a ligand such as a derivative of bipyridine or phe- nanthrol ine. Quenching of the emissions of poly-pyridineruthenium II complexes have been investigated by C. T. Lin et al (Jacs, 98:21 Oct. 1976) to determine the electron and energy transfer mechanisms. The complexes exhibit maximum absorbance around 450 nm and maximum emission around 600 nm and emission lifetimes of 0.001 to 5 microseconds. The absorption and emission spectra of representative complexes in water at 25°C is provided in the following table:

<table>
<thead>
<tr>
<th>Absorption</th>
<th>Emission</th>
<th>( \lambda_{\text{max}} )</th>
<th>( 10^{-2} \times \text{e} )</th>
<th>( \lambda_{\text{max}} )</th>
<th>( \tau_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex</td>
<td></td>
<td>( \text{nm} )</td>
<td>( M^2 \text{cm}^{-1} )</td>
<td></td>
<td>( \mu\text{s} )</td>
</tr>
<tr>
<td>Ru[4(CH_3)H_2py]+[ClO_4]-, 3H_2O</td>
<td></td>
<td>(~430)460</td>
<td>1.43</td>
<td>628</td>
<td>633</td>
</tr>
<tr>
<td>Ru[4(CH_3)H_2py]+Cl_2, 6H_2O</td>
<td></td>
<td>(~445)474</td>
<td>3.27</td>
<td>632</td>
<td>638(653)</td>
</tr>
<tr>
<td>Ru[4(CH_3)H_2py]+Cl_2, 6H_2O</td>
<td></td>
<td>(~433)472</td>
<td>1.46</td>
<td>607</td>
<td>613(627)</td>
</tr>
<tr>
<td>Ru[4(CH_3)H_2py]+Cl_2, 6H_2O</td>
<td></td>
<td>(438)472</td>
<td>2.45</td>
<td>597</td>
<td>605(625)</td>
</tr>
<tr>
<td>Ru[4(CH_3)H_2py]+Cl_2, 6H_2O</td>
<td></td>
<td>(417)440</td>
<td>1.94,1.98</td>
<td>594</td>
<td>605(625)</td>
</tr>
<tr>
<td>Ru[4(CH_3)H_2py]+Cl_2, 6H_2O</td>
<td></td>
<td>(426)534</td>
<td>2.53,2.55</td>
<td>607</td>
<td>613(626)</td>
</tr>
<tr>
<td>Ru[4(CH_3)H_2py]+Cl_2, 6H_2O</td>
<td></td>
<td>(425)534</td>
<td>1.84,2.04</td>
<td>602</td>
<td>608(625)</td>
</tr>
<tr>
<td>Ru[4(CH_3)H_2py]+Cl_2, 6H_2O</td>
<td></td>
<td>(460)540</td>
<td>2.60,2.62</td>
<td>610</td>
<td>612(627)</td>
</tr>
<tr>
<td>Ru[4(CH_3)H_2py]+Cl_2, 6H_2O</td>
<td></td>
<td>(420)540</td>
<td>1.79,1.94</td>
<td>597</td>
<td>605(625)</td>
</tr>
<tr>
<td>Ru[4(CH_3)H_2py]+Cl_2, 6H_2O</td>
<td></td>
<td>(498)417</td>
<td>2.82,2.84</td>
<td>633</td>
<td>607(625)</td>
</tr>
<tr>
<td>Ru[4(CH_3)H_2py]+Cl_2, 6H_2O</td>
<td></td>
<td>(421)447</td>
<td>1.83,1.90</td>
<td>593</td>
<td>605(625)</td>
</tr>
</tbody>
</table>
fused silica, sapphire, ultra pure water. The water may be purified by repeated distillation. By contrast, the emission lifetime of the bipyridine complex is increased by methyl substitution on activated carbon. Furthermore, the solution in fibrous form.

The 4,7-(CH$_3$)phen, 5,6-(CH$_2$)phen, 5-(CH$_3$)phen complexes show appreciable reaction with europium (III). The emission lifetimes are greatly increased by the introduction of phenyl groups in the 4,7 positions of the phenanthroline ring system. However, the lifetimes do not otherwise appear to be especially sensitive to substitution in the 4,7 positions, since the lifetimes of the 4,5 and 5,6 dimethyl derivatives are comparable. Also of interest is the result that introduction of a methyl group in the 4,4'positions of bipyridine decreases the emission lifetime of the complex, whereas the lifetime of the 7,7'-phenanthroline complex is increased by methyl substitution. By contrast, the emission lifetime of the bipyridine and the phenanthroline complexes are both increased by phenyl substitution.

A first embodiment of the invention utilizes a supported Europium(III) photo-oxidant reagent and a soluble photo-reductant regeneration reagent.

Referring now to FIG. 1, the photolytic hydrogen production system includes a photo-oxidation reactor 10 having a face 11 directed towards and transparent to solar radiation 16. The transparent panels utilized in the reactor must be transparent to the full ground level recovered in recovery vessel 10. The introduced light may develop that certain highly turbulent systems in-
when incident solar radiation 206 photolyses the water according to the following reaction:

\[
2\text{Eu}^{(2)} + 2\text{H}_2\text{O} \xrightarrow{\text{photolysis}} 2\text{Eu}^{(3)} + \text{H}_2 + 2\text{OH}^-
\]

Generated hydrogen is collected at outlet 203.

The strongly acidic spent solution 208 is then pumped by means of pump 210 into column 201 with valve 212 open and valve 214 closed. The walls 216 of the column 201 are either covered with a +450nm band pass filter or the walls are fabricated from a material passing the desired wavelengths. The incident solar radiation 206 will generate reductant according to the following reaction:

\[
\text{RuL}_3^{(2+)} + \text{O}_2 \rightarrow \text{RuL}_3^{(3+)} + \text{H}_2 + \text{O}_2
\]

As the spent solution 208 flows over the reductant regeneration occurs as follows:

\[
\text{Eu}^{(2)} + ^*\text{RuL}_3^{(2+)} \rightarrow \text{RuL}_3^{(3+)} + \text{Eu}^{(3+)}
\]

Oxygen is evolved very slowly by RaLuL₃₊(3) from strongly acidic solutions. Therefore by slowly flowing the solution through the column 201, regenerated Eu₊(2) can be conducted away from the fixed RaLuL₃₊(3). By utilizing a sufficiently lengthy column substantially all of the Eu₊(3) is regenerated. No lifetime limitation exists as to Eu₊(2) and hence, spacing of the surfaces of the RaLuL₃ particles can be adjusted to provide an adequate flow rate at low pressure differentials. The regenerated photoxidant solution is recycled to reactor 200 through line 218 with valve 214 closed and valve 220 open.

The cycle is completed by a dark reaction to regenerate the RuLuL₃₊(3) and to generate oxygen. After recycle of the regenerated solution, valve 214 is closed, valve 237 is opened and water at pH 7 is pumped into column 201. A dark cover 232 is placed over the column. The following reaction proceeds.

\[
\text{H}_2\text{O} + 2\text{RuL}_3^{(3+)} \xrightarrow{\text{dark reaction}} 2\text{RuL}_3^{(2+)} + 2\text{H}^+ + \frac{1}{2} \text{O}_2
\]

Oxygen is collected at 234. After complete regeneration the wash water is drained with valve 214 directed toward outlet 236.

In a further embodiment of the invention both the Eu₊(3) photo-oxidant and *RuLuL₃₊(2) photo-reductant are bonded to the surface of a support such as particulate alumina. Control of the pH of the aqueous media is utilized to separate the production of hydrogen and oxygen according to the following reactions.

**Reductant Activation**

\[
\text{RuL}_3^{(2+)} \rightarrow \text{RuL}_3^{(3+)}
\]

**Hydrogen Formation**

\[
\text{RuL}_3^{(2+)} + \text{Eu}^{(+3)} \xrightarrow{\text{photolysis}} \text{RuL}_3^{(3+)} + \text{Eu}^{(+2)}
\]

\[
2\text{Eu}^{(+2)} + 2\text{H}_2\text{O} \xrightarrow{\text{photolysis}} 2\text{H}_2 + \text{O}_2 + \text{OH}^-
\]

The above-recited irradiation steps utilize light in the wavelength range of about 290 to 550 nm.
A method according to claim 6 in which the metal concentration of the recombination catalyst is 0.5 to 0.005% by weight.

8. A method according to claim 1 in which the reagent is a transition metal cation selected from Eu++, Cr++, V++ and Ti++ and the pH of the solution is no more than 5.

9. A method according to claim 8 in which the solution further contains 0.5 to 5M of Cl-, SO4²⁻ or PO4³⁻.

10. A method according to claim 8 in which the cation is Eu++ and the wavelength of solar radiation is <400 nm.

11. A method according to claim 1 in which the regenerant is a ruthenium pyridine or phenanthroline complex in a photoexcited state.

12. A method according to claim 11 further including the step of reacting a ruthenium (+3) ligand complex with water to form ruthenium (+2) ligand regenerant precursor and oxygen and further including the step of exposing the precursor to solar radiation at a wavelength greater than 450 nm to form photoexcited regenerant.

13. A method according to claim 1 in which the reagent is deposited on a support and further including the step of flowing a solution of regenerant over the supported spent reagent.

14. A method according to claim 1 in which the regenerant is deposited on a support and further including the step of flowing a solution of spent reagent in contact with the supported regenerant.

15. A method according to claim 1 in which both the reagent and regenerant are deposited on a support disposed in a reactor and further including the step of irradiating water in the reactor at pH ≤ 5 at a wavelength of 290 to 550 nm followed by a dark reaction of water at a pH of about 7.

** ** ** ** **