

ELECTROCATALYTIC HYDROGEN CARRIER COMPOSITIONS

FIELD OF INVENTION

0001. The present disclosure relates to hydrogen storage via liquid organic hydrogen carriers, as well as to electrochemical cells, batteries and fuel cells that use hydrogen fuel. More specifically, the instant invention relates to liquid organic hydrogen carrier compositions for processing via electrochemical methods.

BACKGROUND

0002. Hydrogen is one net-zero fuel being adopted widely as replacement of traditional fossil fuels due to its production pathways often being from renewable resources, its clean nature, its high energy density and its nature of being a sustainable transportable energy source. Hydrogen can be used in many applications to generate electricity, power or heat, by powering fuel-cell electric vehicles or stationary energy systems. Hydrogen storage is a key enabling technology for the deployment of hydrogen and fuel cell technologies and the acceleration of clean power adoption around the world. Hydrogen has the highest energy per mass of any fuel. However, due to its low volumetric density of hydrogen, storage of hydrogen is one of the key barriers for its widespread use in portable and stationary applications

0003. The realization of high-density hydrogen storage is a significant challenge for portable and stationary applications as well as long-distance transportation applications. Presently available techniques are typically based on the storage of gaseous hydrogen that requires large-volume systems resulting in a critical issue for portable applications. Over the past decade, extensive investment in hydrogen storage research and commercial development has created commercially-available solutions in which hydrogen is chemically bonded with the molecules of solid/liquid materials, such as metal-hydrides and liquid organic hydrogen carriers (LOHCs).

0004. Hydrogen storage in LOHCs is a promising technology that enables the safe storage of hydrogen in the absence of extremely high pressures and/or temperatures for long durations and with a volumetric hydrogen storage density comparable to cryogenic

liquified hydrogen. The similar properties of LOHC and crude oil derivatives at ambient conditions allows for transportation of hydrogen at high storage densities in LOHC using existing gasoline and diesel fueling infrastructure which results in reduced operational costs compared to compressed or liquid hydrogen.

0005. Liquid organic hydrogen carrier (LOHC) refers to a chemical compound that can absorb and release hydrogen through chemical reactions. Such compounds include at least partially unsaturated hydrocarbons (aka lean LOHC) which undergo hydrogenation, for example, at a H₂-source site, to provide a storable and transportable fluid in the form of corresponding (more) saturated hydrocarbons (aka rich LOHC). The saturated hydrocarbons can be dehydrogenated to release hydrogen at the site of use and to form a hydrogen depleted fluid comprising at least partially unsaturated hydrocarbons, which is transferred to a hydrogen source site where it is converted to its saturated form by hydrogenation processes. Typical carrier fluids are the “molecule pairs” in their hydrogenated and dehydrogenated forms, for example, cyclohexane/benzene, methyl cyclohexane/toluene, cyclohexanol/phenol; decalin/naphthalene, butanol/butanone, cyclohexanol/cyclohexenol, cyclohexanol/cyclohexenone, etc.
0006. The storage and release of hydrogen in LOHC are based on a two-step cycle of hydrogenation and dehydrogenation through thermo-catalytic or electro-catalytic reactions. Unlike the thermo-catalytic hydrogenation and dehydrogenation of LOHC that requires relatively higher pressures and temperatures, electro-catalytic reactions can take place at ambient conditions through a simpler and potentially more efficient process. This makes electro-catalytic LOHC systems that are powered by electrical energy a suitable rechargeable storage system for off-grid and decentralized hydrogen applications.
0007. In a typical LOHC system, a lean-LOHC reacts with hydrogen during hydrogenation to produce a rich-LOHC, while the reverse occurs during dehydrogenation. In an electrochemical system, this can be further described via half reactions occurring at the anode and cathode as follows, where X is defined by the number of hydrogen moieties added/removed from the LOHC during hydrogenation/dehydrogenation respectively.

Hydrogenation



Half reactions:

Oxidation $\text{XH}_2 \rightarrow 2\text{X H}^+ + 2\text{X e}^-$

Reduction: $2\text{XH}^+ + 2\text{Xe}^- + \text{lean-LOHC} \rightarrow \text{rich-LOHC}$

Dehydrogenation

$\text{Rich-LOHC} \rightarrow \text{lean-LOHC} + \text{XH}_2$

Half Reactions:

Oxidation: $\text{Rich-LOHC} \rightarrow 2\text{X H}^+ + 2\text{Xe}^-$

Reduction: $2\text{XH}^+ + 2\text{Xe}^- \rightarrow \text{XH}_2$

0008. Electrochemical reactors have been deployed in the generation of hydrogen gas via electrolysis and in industrial processing (e.g. water treatment). These electrochemical storage systems provide stable, low-energy storage of hydrogen, but are limited in application by the low density of the stored hydrogen.
0009. Application of electrochemical transformations for hydrogen transportation in solution has been explored much less. In recent reports from Yokohama National University, toluene hydrogenation via polymer electrolyte membrane (PEM) electrochemical reactors was explored (Fukazawa et al., *Bull. Chem. Soc. Jpn.*, 2018, 91 (6) pp. 897-899, Takano, et al., *Bull. Chem. Soc. Jpn.* 89 pp. 1178–1183, 2016). These early reports have limited scope in demonstration of full LOHC transformations and/or stable performance.
0010. Therefore, there is a need for improved hydrogen storage and release systems, and hydrogen carriers designed for electrochemical reactors that can overcome one or more of the limitations of the existing technologies.
0011. This background information is provided for the purpose of making known information believed by the applicant to be of possible relevance to the present invention. No admission is necessarily intended, nor should be construed that any of the preceding information constitutes prior art against the present invention.

SUMMARY OF THE INVENTION

0012. An object of the present invention is to provide hydrogen carrier fluid compositions

designed for hydrogen storage and release in systems and methods utilizing electrochemical reactors.

0013. In accordance with an aspect of the present invention, there is provided a hydrogen carrier fluid (HCF) composition, comprising a) a lean-liquid organic hydrogen carrier (lean-LOHC) component comprising at least one cyclohexyl-based compound having at least one unsaturated bond, optionally in combination with one or more C₄₋₁₂ alkyl alcohol, or a rich-liquid organic hydrogen carrier (rich-LOHC) component comprising at least one cyclohexyl-based compound, optionally in combination with a C₄₋₇ ketone, a C₄₋₆ lactone or a mixture thereof; and b) an electrolyte component.
0014. In accordance with another aspect of the present invention there is provided use of the HCF compositions described herein for storage and release of hydrogen, in an electrochemical reactor system.

BRIEF DESCRIPTION OF THE DRAWINGS

0015. Further features and advantages of the present disclosure will become apparent from the following detailed description, taken in combination with the appended drawings, in which:
0016. Fig. 1 schematic depiction of the hydrogenation and dehydrogenation reaction of the LOHC components of the hydrogen carrier fluid (HCF) composition in accordance with an embodiment of the present invention.
0017. Figs. 2 depicts a cyclic voltammogram relating to electrochemical dehydrogenation of a LOHC component in accordance with an embodiment of the present invention.
0018. Fig. 3 depicts a linear scan voltammogram relating to electrochemical dehydrogenation of a LOHC component in accordance with an embodiment of the present invention.
0019. Fig. 4 depicts a cyclic voltammogram relating to electrochemical dehydrogenation of a LOHC component in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION

0020. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.
0021. Unless the context requires otherwise, throughout this specification and claims, the words “comprise”, “comprising” and the like are to be construed in an open, inclusive sense.
0022. The articles “a” and “an” are used herein to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article. By way of example, “an element” means one element or more than one element.
0023. As used herein, the term “about” refers to approximately a +/-10% variation from a given value. It is to be understood that such a variation is always included in any given value provided herein, whether or not it is specifically referred to.
0024. The present invention provides hydrogen carrier fluid (HCF) compositions for use with an electrocatalytic reactor system to enable hydrogenation/dehydrogenation reactions in a method/system for hydrogen storage and release.
0025. In one aspect, the present invention provides a hydrogen carrier fluid (HCF) composition, which comprises a lean-liquid organic hydrogen carrier (lean-LOHC) component optionally in combination with one or more C₄₋₁₂ alkyl alcohol, or a rich-liquid organic hydrogen carrier (rich-LOHC) component optionally in combination with a C₄₋₇ ketone, a C₄₋₆ lactone or a mixture thereof; and an electrolyte component.
0026. The lean-liquid organic hydrogen carrier (lean-LOHC) component comprises at least one cyclohexyl-based compound having at least one unsaturated bond.
0027. The rich-liquid organic hydrogen carrier (rich-LOHC) component comprises at least one cyclohexyl-based compound.

0028. The term "cyclohexyl-based compound", as used herein refers to a monocyclic compound or a fused rings compound, either of which may be optionally substituted with one or more OH and/or alkyl groups.
0029. The fused ring cyclohexyl-based compound can have at least two fused cyclohexyl rings, or a cycloalkyl ring and a 5- or 6-membered heterocycle having at least one hetero atom, such as N, O or S, wherein the cyclohexyl ring can be optionally substituted with one or more of OH and C1-C6 alkyl groups.
0030. Substituent groups of the cyclohexyl ring can be further optionally substituted with cyclohexyl or 5- or 6-membered N-heterocycle group.
0031. Non-limiting examples of cyclohexyl-based compound suitable for use in the rich-LOHC component include cyclohexane, methylcyclohexane, decalin, cyclohexanol, decahydro-N-alkyl carbazole, alkyl-perhydro indole, etc.
0032. Non-limiting examples cyclohexyl-based compound suitable for use in the lean-LOHC component having at least one unsaturated bond include a cyclohexene, a cyclohexanol, benzene, toluene, naphthalene, phenol, benzyl toluene, dibenzyltoluene, biphenyl, N-alkyl carbazole, alkyl indole, etc.
0033. In some embodiments, the rich-LOHC component comprises cyclohexane, methylcyclohexane, cyclohexanol or a mixture thereof. In some embodiments, the rich-LOHC component comprises cyclohexanol or methylcyclohexane.
0034. In some embodiments, the lean-LOHC component comprises a cyclohexene, a methyl cyclohexene, a cyclohexenol, a cyclohexanone, phenol or a mixture thereof. In some embodiments, the lean-LOHC component comprises phenol.
0035. In some embodiments, the lean-LOHC component comprises a methyl cyclohexene, toluene or a mixture thereof. In some embodiments, the lean-LOHC component comprises phenol.
0036. The alcohol suitable for use in the lean-LOHC component can be a C₄₋₁₂ mono- hydroxy

alkyl alcohol, a C₄₋₁₂ poly-hydroxy alkyl alcohol, or a mixture thereof.

0037. In some embodiments, the alcohol is n-butanol, 2-butanol, n-pentanediol, 2-pentanol, 3-pentanol or a mixture thereof. In some embodiments, the alcohol is n-butanol.
0038. In some embodiments, the ketone suitable for use in the rich-LOHC component is butanone, pentanone, pentanedione, or a mixture thereof.
0039. In some embodiments, the ketone is butanone, pentandione or a mixture thereof. In some embodiments, the lactone is gamma-butyrolactone, delta-valerolactone or a mixture thereof. In some embodiments, the lactone is delta-valerolactone.
0040. The electrolyte component suitable for use in the HCF composition can comprise an alkali metal salt, an alkaline earth metal salt, an ammonium salt, C₆₋₁₄ alkyl-C₆₋₁₀ aryl sulfonic acid, or a mixture thereof.
0041. In some embodiments, the electrolyte component comprises an alkali metal salt, an alkaline earth metal salt, an ammonium salt, or a mixture thereof.
0042. In some embodiments, the alkali metal is lithium, sodium or potassium.
0043. The ammonium component of the ammonium salt can be defined as NR₄⁺, wherein R is independently selected from H or one or more C₁₋₄ alkyl groups.
0044. Non-limiting examples of a counter ion of the alkali metal salt, the alkaline earth metal salt, or the ammonium salt is hydroxide anion, perchlorate anion, borate anion, carbonate anion or acetate anion.
0045. In some embodiments, the electrolyte component is an alkali or alkaline earth metal perchlorate. In some embodiments, the electrolyte component is lithium perchlorate.
0046. In some embodiments, the electrolyte component is tetrabutyl ammonium hydroxide. In some embodiments, the electrolyte component is dodecylsulfonic acid.

0047. In some embodiments, the HCF composition further comprises a transition or post transition metal complex.
0048. In some embodiments, the transition metal is Pd, Ru, V, Fe, Mn or Ni. In some embodiments, the post transition metal is Al.
0049. In some embodiments, the transition metal complex is Pd-pivalate (Pd- trimethylacetate).
0050. In some embodiments, the HCF composition further comprises an organic redox mediator.
0051. The term "organic redox mediator" or "catalyst" used herein includes compounds that form stable organic radicals that act as intermediate electron carriers or reservoirs without changing final products of the electrochemical reaction of LOHCs. These compounds regenerate at the electrode surface.
0052. Non limiting examples of organic redox mediators include quinones (such as benzoquinone, 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone, naphthoquinone), TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), N-hydroxyphthalimide, C₁₋₆ trialkylamine, C₁₋₆ dialkylamine, C₁₋₈ diamine, etc.
0053. In some embodiments, the organic redox mediator is triethylamine, *N,N'*-Dimethyl-1,3-propanediamine, or N-hydroxyphthalimide.
0054. In some embodiments, the HCF composition comprises a solvent medium. In some embodiments, the solvent medium is water.
0055. The HCF composition can comprise up to about 90% by weight of the lean-LOHC component, up to 60% by weight of the alcohol, up to about 20% by weight of the electrolyte component, and up to 5% by weight of the transition metal or post transition metal complex/compound, and up to 5% by weight of the redox mediator.
0056. In some embodiments, the composition comprises about 40wt%-90wt% of rich-LOHC component, about 20wt%-60wt% of ketone, lactone or mixture thereof, about 1wt%-20wt% of electrolyte component, about 0.5wt%-5wt% of the transition metal or post

transition metal complex/compound, and about 0.5wt%-5wt% of the redox mediator.

0057. Without being bound by a theory, it is believed that the alcohol may act as a dispersant and/or liquid organic hydrogen carrier; and the electrolyte component may act to mitigate capacitive charge generation.
0058. In some embodiments, the alcohol acts as a hydrogen carrier and is reversibly dehydrogenated/hydrogenated between the alcohol and ketone or lactone forms, e.g. butanol to butanone, pentanediol to gamma-valerolactone or pentanedione.
0059. In another aspect, the present invention provides use of the HCF composition for storage and release of hydrogen in electrocatalytic reactor systems/methods.
0060. When used in electrocatalytic reactor systems and methods, the LOHC components of the HCF compositions of the present invention can be cycled between a hydrogenated form (rich-LOHC) and a dehydrogenated form (lean-LOHC), using a hydrogenation reactor (H-Reactor) and a dehydrogenation reactor (D-Reactor).
0061. The HCF compositions may be transported via pipeline, truck, train or personal tanks depending on end-use applications. The lean-LOHC may be re-hydrogenated at a facility or hydrogen re-fueling hub. The rich-LOHC may be used on-site for the generation of hydrogen fuel for end application in electrical power generation, heating, or other hydrogen gas end-use cases.
0062. In some embodiments, the LOHC of the HCF composition of the present invention can be electrochemically dehydrogenated in a dehydrogenation reactor (D-reactor) comprising an anode and a cathode to generate a lean-LOHC.
0063. In some embodiments, the HCF composition of the present invention is transformed on-site to generate a hydrogen fuel via the D-Reactor.
0064. In some embodiments, the HCF composition of the present invention is transported to a site of the D-reactor via pipeline, concentric pipeline, tanker, personal-use tanks, concentric personal-use tanks, or similar methods.

0065. In some embodiments, the lean-LOHC of the HCF composition is returned for hydrogenation via pipeline, concentric pipeline, tanker, personal-use tanks, concentric personal-use tanks, or similar methods.
0066. In some embodiments, the lean-LOHC is re-hydrogenated at a re-fueling hub, or a similar center, via use of a hydrogenation reactor (H-reactor).
0067. Although the invention has been described with reference to certain specific embodiments, various modifications thereof will be apparent to those skilled in the art without departing from the spirit and scope of the invention. All such modifications as would be apparent to one skilled in the art are intended to be included within the scope of the following claims.
0068. To gain a better understanding of the invention described herein, the following examples are set forth. It will be understood that these examples are intended to describe illustrative embodiments of the invention and are not intended to limit the scope of the invention in any way.

Examples

0069. **Fig. 1** depicts a LOHC system involving the LOHC compounds of the present invention, wherein a lean-LOHC (i.e. benzene) and a ketone or lactone reacts with hydrogen during hydrogenation, to produce a rich-LOHC (i.e. cyclohexane) and an alcohol during hydrogenation, while the reverse occurs during dehydrogenation, wherein the cyclohexane is converted back to a cyclohexene and/or benzene, and alcohol is converted to the ketone or lactone.

Example 1

0070. An electrocatalytic HCF formulation comprising a mixture of 1:1 by volume of methylcyclohexane and butanol, with 0.1 M tetrabutyl ammonium hydroxide was used in a parallel flow electrochemical reactor. The electrodes were composed of a Ni metal foam coated with a platinum group metal catalyst. The electrodes were connected to a power source, such that adjacent electrodes acted as a monopolar anode and cathode, with a 0.3 mm spacing between electrodes and a nylon based flow distributor. The applied

potential was ramped to 2.5V at a rate of 0.2V/s. Electrochemical oxidation of the methylcyclohexane and butanol was established as an increase in current above 0.75V, with the anodic reaction being the oxidation of the liquid organic hydrogen carrier(s), and the cathodic reaction being hydrogen evolution reaction (Figure 2).

0071. This system was operated under chronoamperometric conditions with a fixed current of 20mA and an average applied potential of 2.6V for 2.5h, yielding conversion of the butanol to butanone (>2%) and the methylcyclohexane to methylcyclohexene (<1%) with release of hydrogen gas at the cathode.

Example 2

0072. An electrocatalytic HCF formulation comprising a mixture of 40ml each n-butanol and methylcyclohexane, 16g 4-dodecylbenzenesulfonic acid and 0.15g Pd-pivalate was used in a beaker style electrochemical reactor. The working and counter electrodes were composed of Ni metal foam coated with a platinum group metal catalyst. The pseudo reference electrode was a silver wire. The electrodes were connected to a potentiostat (Admiral Ace), such that the electrodes acted as a monopolar anode and cathode, with a 3-5 mm spacing between electrodes. The applied potential was ramped from -0.15V to 1.5V at a rate of 0.2 V/s. Electrochemical oxidation of the methylcyclohexane and butanol was established as an increase in current beginning at -0.15V, with the anodic reaction being the oxidation of the liquid organic hydrogen carrier(s), and the cathodic reaction being hydrogen evolution reaction (Figure 3). A leveling of current at 1.6mA is observed at potentials greater than 0.2V vs Ag pseudo reference due to mass transport limitations for one or more species. This system was operated under chronoamperometric conditions with a fixed current of 1mA and an average applied potential of 1V for 4h, yielding conversion of the butanol to butanone (>5%) and the methylcyclohexane to methylcyclohexene (~1%) with release of hydrogen gas at the cathode which was vented to the atmosphere in a laboratory fumehood.

Example 3

0073. An electrocatalytic HCF formulation comprising 30 mg cyclohexanol, 0.5 M lithium perchlorate and 8 mg the redox mediator N-hydroxyphthalimide was diluted in 1.5 ml acetonitrile and tested in a beaker style electrochemical reactor. The electrodes were composed of a graphite rod with a platinum group metal catalyst. The electrodes were

connected to a power source, such that adjacent electrodes acted as a monopolar anode and cathode, with a 0.2 mm spacing between. The applied potential was ramped to 2V at a rate of 0.05 V/s. Electrochemical oxidation of the cyclohexanol was established as an increase in current above 1.1V, with the anodic reaction being the oxidation of the liquid organic hydrogen carrier(s), and the cathodic reaction being hydrogen evolution reaction (Figure 4, HCF with mediator). For comparison, the system was tested with the same electrochemical scanning profile without the addition of the redox mediator (Figure 4, HCF without mediator). This scan shows a significant shift in the onset of oxidation (indicated by an increase in current) from ~1V to >1.5V, highlighting the catalytic behavior of the redox mediator for electrochemical HCF oxidation. This system was operated under chronoamperometric conditions with a fixed current of 2mA and an average applied potential of 1.8V for 0.75 h, yielding conversion of the cyclohexanol to cyclohexanone/cyclohexenol (>10%), cyclohexenone <1%, phenol <0.1%.

We Claim:

1. A hydrogen carrier fluid (HCF) composition, comprising:
 - a) a lean-liquid organic hydrogen carrier (lean-LOHC) component comprising at least one cyclohexyl-based compound having at least one unsaturated bond, optionally in combination with one or more C₄₋₁₂ alkyl alcohol, or a rich-liquid organic hydrogen carrier (rich-LOHC) component comprising at least one cyclohexyl-based compound, optionally in combination with a C₄₋₇ ketone, a C₄₋₆ lactone or a mixture thereof; and
 - b) an electrolyte component.
2. The HCF composition of claim 1, wherein the rich-LOHC component comprises cyclohexane, methylcyclohexane, cyclohexanol or a mixture thereof.
3. The HCF composition of claim 1, wherein the lean-LOHC component comprises a cyclohexene, a methyl cyclohexene, a cyclohexenol, a cyclohexanone, phenol or a mixture thereof.
4. The HCF composition of any one of claims 1 to 3, wherein the alcohol is butanol, pentanediol, or a mixture thereof.
5. The HCF composition of any one of claims 1 to 3 wherein the ketone is butanone, pentandione, or a mixture thereof, and the lactone is delta-valerolactone.
6. The HCF composition of any one of claims 1 to 5 wherein the electrolyte component comprises an alkali metal salt, an alkaline earth metal salt, an ammonium salt, C₆₋₁₄ alkyl-C₆₋₁₀ aryl sulfonic acid or a mixture thereof.
7. The HCF composition of claim 6, wherein a counter ion of the alkali metal salt, the alkaline earth metal salt, the ammonium salt is hydroxide anion, perchlorate anion, borate anion, carbonate anion or acetate anion.
8. The HCF composition of claim 6, wherein the electrolyte component is dodecylsulfonic acid.

9. The HCF composition of any one of claims 1 to 8, further comprising a transition metal complex or post transition metal complex.
10. The HCF composition of claim 9, wherein the transition metal is Pd, Ru, V, Fe, Mn, or Ni, and the post transition metal is Al.
11. The HCF composition of claim 10, wherein the transition metal complex is Pd-pivalate (Pd-trimethylacetate).
12. The HCF composition of any one of claims 1 to 11, further comprising an organic redox mediator.
13. The HCF composition of claim 12, wherein the organic redox mediator is benzoquinone, naphthoquinone, N-hydroxyphthalimide, triethylamine, *N,N'*-Dimethyl-1,3-propanediamine or TEMPO.
14. The HCF composition of any one of claims 1 to 8, wherein the composition comprises:
about 40wt%-90wt% of the lean-LOHC component;
about 20wt%-60wt% of the alcohol; and
about 1wt%-20wt% of the electrolyte component.
15. The HCF composition of any one of claims 1 to 8, wherein the composition comprises:
about 40wt%-90wt% of the rich-LOHC component;
about 20wt%-60wt% of the ketone, the lactone or a mixture thereof; and
about 1wt%-20wt% of the electrolyte component.
16. The HCF composition of claim 14 or 15, further comprising:
about 0.5wt%-5wt% of the transition metal complex or post transition metal compound/complex; and/or
about 0.5wt%-5wt% of the redox mediator.
17. Use of the HCF composition as defined in any one of claims 1 to 16 for storage and release of hydrogen.